Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

MERCURY, LIQUID AND SOLID, UNDER PRESSURE.

By P. W. Bridgman.

Presented by G. W. Pierce, Oct. 11, 1911. Received Oct. 6, 1911.

Introduction.

This paper is an attempt to present for the liquid and solid phases of a single simple substance, mercury, data corresponding to the data which have been collected for the gaseous and liquid phases of many substances. These latter data are the relations connecting temperature, pressure, and volume of the gas together with the changes involved when the gas passes to the liquid state. Out of these data have come the theories of the molecular structure of gases and vapors, and the various relations connecting the gaseous with the liquid phase, of which the theory expressed by the equation of van der Waals is the best known. The corresponding work for the liquid and solid phases, that is, the mapping out of the pressure-volume-temperature surface of the liquid and the determination of the quantities involved in the change from the liquid to the solid state, has never been done. As a result, the theory of liquids is entirely undeveloped, and the theory of the relation between liquid and solid hardly begun. For instance, the fundamental question as to the existence of a critical point for the liquid-solid states analogous to that for the vapor-liquid is as yet unsettled.

The apparent reason for this neglect of the thermodynamic data for the liquid and solid is merely experimental difficulty. Whereas for a vapor the critical pressure never exceeds a few hundred atmospheres, the pressures involved in a corresponding study of the liquid-solid phases are of the order of tens of thousands of atmospheres. These pressures are so high as to tax to the utmost the tightness of every joint and the strength of the steel vessels. In this present work it has been found possible by a special packing device, which secures absolute freedom from leak, and by the use of the highest grades of steel manufactured, to reach 30,000 and even 40,000 atmos on the first application of pressure. On subsequent applications rupture may come at half the first maximum. This subsequent early rupture is due to the fact that these pressures are greatly in excess of the theoretical limit of the steel, so that there is a distortion of the inner parts far beyond the elastic limit and consequent rapid fatigue. The pressures reached in this paper are not the greatest attainable because of the questionable scientific economy of pushing pressures to a value where rupture may occur at any moment and destroy valuable apparatus and time.

The previous work in this field is wholly below 5000 kgm. The two principal investigators are Amagat,[1] who studied the compressibility and the thermal dilatation of a number of liquids up to 3000 atmos, without, however, touching on the change of state liquid-solid; and Tammann,[2] who studied the change of state liquid-solid, without determining the behavior of the liquid, over a range of pressure of usually about 3000 kgm., but reaching a few times to 4000 and once to 4800. There are no liquids common to the work of both Amagat and Tammann, so that the complete data are not known for even a single liquid.

The previous work done on mercury is almost negligible for the present purpose. Accurate compressibility determinations run only to 500 kgm. (the highest are by Richards [3]), and the effect of pressure on freezing point has been observed only by Tammann, [4] who found results up to 2000 kgm. that are inconsistent among themselves by 30 per cent.

The data of this paper cover a range of 12,000 kgm., and give both the changes of volume of the liquid with temperature and pressure, and the thermodynamic data required on the freezing curve. The temperature range corresponding to this wide pressure range is comparatively small, since at 12,000 kgm. the freezing temperature has been raised to only 20°, that is, through a range of 60°.

In addition to the data connected more intimately with pressure, several quantities relating to solid mercury at atmospheric pressure have incidentally been determined. It has been a surprise to find how untrustworthy the commonly accepted data for solid mercury are. Thus the only determination of the latent heat of melting dates back to 1838, before the value of the melting temperature itself was known more accurately than within 3°.

---

[1] Amagat, Ann. de Chim. et Phys. (6), **29**, 68–136, 505–574 (1893).

[2] Tammann, Kristallisieren und Schmelzen (Barth, Leipzig, 1903).

[3] Richards, Pub. Carnegie Inst. Wash., No. 7 (1903), and No. 76 (1907).

[4] Tammann, loc. cit., p. 248.

The experimental material of the paper, with respect to both subject matter and experimental method, falls naturally into two parts. The first is concerned with the p-v-t surface of the liquid. To map this the isothermal compressibility of the liquid was found at two temperatures, 0° and 22°, and combined with the known dilatation at atmospheric pressure. This is sufficient to cover the region in question, because the change of dilatation with temperature is slight. The second part is concerned with the changes taking place on the freezing curve. Thermodynamically, the data required are the change of volume on passing from liquid to solid and the variation of freezing temperature with pressure. From these the latent heat may be calculated by Clapeyron's equation. Two independent methods were used; one which gave both the change of volume and the relation between temperature and pressure on the freezing curve, and another which gave only the freezing curve. In addition still another method was used in determining the change of volume on freezing at atmospheric pressure.

In the conclusion, the data collected are discussed from the point of view of their bearing on present theories of the liquid state, and the change solid-liquid. These data for a single substance cannot justify by any means an attempt at a new theory. This is simply a first step, indicating in a general way the nature of the effects to be expected at high pressures. From this point of view there are considerations both for and against the use of mercury. On the one hand, the compressibility and thermal dilatation of mercury are comparatively small, so that the change in these quantities under the pressure range employed is not nearly as great as it would be for many organic liquids; but on the other hand, the internal structure of mercury is probably at least as simple as that of any other known substance, so that in the liquid state the results are not complicated by entrance of polymerization, and on the freezing curve the results are not complicated by the entrance of allotropic forms, as they are in the case of water, for example.

The discussion of the methods and the possibilities of error has necessarily been somewhat minute and painstaking. It is hoped that this will be pardoned when it is realized that the field in which these measurements are made has been hitherto practically unworked, and is one where there are several unusual sources of error to be guarded against. At the same time it is a field in which, by the exercise of proper precautions, an accuracy equal to that of the greater number of physical measurements can be reached. The accuracy of nearly all of the following measurements is of the order of 1/10 per cent.

CONTENTS.

- I. Introduction 347
- II. The P–V–T Surface of Liquid Mercury 351
  - *a.* Nature of the Experimental Problem — Difficulties in Measuring Compressibility at High Pressures 351
  - *b.* Description of the New Method 354
    - Formulae 357
    - Details of Manipulation 358
    - Compressibility of the Steel Piezometers 362
      - Discussion of the Method 362
        - Hysteresis in the Containing Cylinder 364
      - The New Values up to 10,000 kgm.—Temperature Coefficient 366
        - Comparison with Other Results 367
  - *c.* Data on the Compressibility of Mercury 368
    - The Method of adjusting the Data 369
    - Comparison with Other Results 376
  - *d.* Discussion of the Results 380
    - Compressibility as a Function of Pressure and Temperature 381
    - Dilatation as a Function of the Pressure 382
      - Variation with Temperature Imperceptible 380
    - The Specific Heats 383
    - The Adiabatic Compressibility 384
    - The Heat of Compression 384
    - Changes of Internal Energy 386
- III. The Change of State, Liquid-Solid 387
  - *a.* The Thermodynamic Data needed — Methods 387
  - *b.* Co-ordinates of the Freezing Curve by Change of Resistance 388
    - Method and Details of Manipulation 388
    - Data — Method of Adjusting the Values 393
    - Incidental Data during Resistance Measurements 394
      - Electrical Resistance of Liquid Mercury under Pressure 395
      - Electrical Resistance of Solid Mercury — Change Solid to Liquid 395
      - Rough Value for Pressure Coefficient of Resistance of Solid 396
      - Comparison with Previous Values for the Resistance of the Solid 397
      - Resistance of an Amalgam under Pressure 398
  - *c.* The Melting Curve by the Change of Volume Method 399
    - The Method 399
    - The Apparatus 400
      - Order of Procedure 401
    - Detailed Discussion of Possible Errors 402
      - Leak 402
      - Elastic After-Effects 402
      - Elastic Deformation — Calculation of Correction 406
      - Temperature Corrections 408
      - Thermal Dilatation of the Transmitting Liquid 410

Change of State of the Transmitting Liquid 413
Measurements of Piston Displacement 413
Pressure Measurements 414
The Data 414
Methods of Computation 416
The Latent Heat — New Value at Atmospheric Pressure . 420
. Recomputed Value for the Specific Heat of the Solid . 422
Rough Value for the Compressibility of the Solid 423
d. Change of Volume at Atmospheric Pressure 423
Probable Error in the Previous Results 424
The New Method 424
The New Value 428
Recomputation of Quantities depending on the Value for the Change of Volume 428
Density of the Solid 428
Dilatation of the Solid 428
Direct Experimental Evidence on this Point 429
e. Subcooling and Superheating 429
IV. Conclusion 431
Bearing on the Theory of Liquids 432
Bearing on the Theory of the Change of State, Liquid-Solid . . 433
Significant Behavior of Latent Heat and Internal Energy. . . 435
V. Summary 437

THE P-V-T SURFACE OF MERCURY.

The Compressibility of Liquid Mercury.

This first section of the paper is devoted to a determination of the compressibility of mercury at 0° and at 22°. The question of experimental method is important, since the compressibility of mercury is small, and there are various effects which make determinations at high pressures much more difficult than over a smaller pressure range. The section comprises a discussion of the method and the various errors to be avoided, an experimental determination of the compressibility of the steel, which was needed in the computations, the actual data for the compressibility of mercury, with a somewhat detailed discussion of the way of adjusting them so as to give the best results, and finally, a calculation from the data of the change of the various physical properties of mercury under pressure.

One of the chief difficulties in the experimental investigation of the properties of bodies under pressure is the determination of the correction for the distortion of the containing vessel. This is particularly true in the case of compressibility, where the change of shape and volume of the containing vessel is an effect of the same kind as that being measured, and may often constitute a large part of the total change.

To correct for the distortion of the containing vessel only indirect methods are open, as direct observation of the vessel under high pressure is out of the question. All of those indirect methods which are primary, that is, which do not assume the correctness of the work of some other observer, endeavor to determine in one way or another the compressibility of the material of the containing vessel. This may be done by measuring Young's modulus and the bending or the torsion coefficient, and from these calculating the cubic compressibility by the identical relations of the theory of elasticity; or it may be done with the introduction of less questionable assumptions by measuring the linear compressibility and then multiplying by three for the cubic compressibility. This latter method in somewhat different forms has been adopted by Richards[5] and the author.[6] Once the compressibility is known, the change of volume of the vessel is found immediately by multiplying the compressibility by the pressure. This assumes that the containing vessel changes volume without changing shape. This assumption, which is made universally, seems necessary and unavoidable. There can be little question, however, that the assumption is not entirely justified. There are outstanding discrepancies between the determination of the same compressibility by different observers, or by the same observer with different apparatus, or indeed by the same observer with the same apparatus on different occasions, that are beyond the limits of error of the measurements. For instance, four very careful determinations of the compressibility of mercury by de Metz[7] differed among themselves by 5 per cent. The containing vessels were all of the same kind of glass, and the elastic constants had been determined by direct experiment. The only explanation of these discrepancies seems to be that the distortion of the containing vessel is irregular, so that there is change of shape as well as change of volume. The irregularities in the results introduced by irregularities in the piezometer will, of course, be proportional to the total correction introduced by the envelope, and will be greatest in the case of the most incompressible liquids. Thus for mercury in a glass envelope, the correction for the envelope is 60 per cent of the whole effect, while for water it is only 5 per cent.

There can be no doubt that these irregularities are due to lack of homogeneity in the containing vessel, either imperfect annealing or actual variation in the constitution of the material from point to point. It is inconceivable that a perfectly homogeneous body of any shape, when exposed to purely hydrostatic pressure, should suffer anything except mere change of volume without change of shape. If, however, the substance be heterogeneous, so that the elastic constants vary from point to point, then the application of hydrostatic pressure will be followed by change of shape, yielding of one part at the expense of another. If the pressure is high enough, it is conceivable that the elastic limit may be exceeded in some places and not in others, resultingin greatly exaggerated change of shape. Even if the elastic limit is not exceeded, there are other effects which will produce irregular action, such as elastic after-effects and hysteresis, and these effects become rapidly more prominent at high pressures. It follows, therefore, that the irregularities of compressibility determinations over a wide pressure range are going to be more than proportionally greater than the irregularities over a narrow range.

---

[5] Richards, loc. cit., 1907.

[6] Bridgman, These Proceedings, **44**, 255–270 (1909).

[7] De Metz, Wied. Ann., **47**, 706–742 (1892).

All previous determinations of compressibility have been made under fairly favorable conditions. The work to the highest pressures has been done by Amagat, to 3000 atmos, in which he determined the compressibility of the compressible liquids in a glass envelope. His determinations of the compressibility of the most incompressible liquid, mercury, were only to 50 atmos. The highest accurate work on mercury seems to have been done by Richards to 500 atmos, a comparatively low pressure. Richards also used glass piezometers. The highest previous work of any sort on mercury seems to have been done by Carnazzi,[8] to 3000 atmos, also with a glass piezometer. His accuracy was not such as to justify more than two figures in the final result.

In determining the compressibility of mercury to pressures as high as 12,000 kgm., as it was desired to do in this paper, we have conjunction of the causes most unfavorable to accuracy; low compressibility of the liquid, and greatly exaggerated irregularity in the distortion of the containing vessel. The employment of a glass containing vessel would seem to be out of the question. In a previous paper,[9] the linear compressibility of glass has been determined directly to 6800 kgm. Over this lower range, irregularities were found amounting to 4 per cent. In using a glass piezometer, this irregularity would be magnified by the fact that the compressibility of glass is high compared with that of the mercury. The ideal substance is one which can be obtained in a state of great homogeneity, and which at the same time has as low a compressibility as possible. Steel has these properties in a higher degree than any other substance, the compressibility being as low as any except the platinum metals, and the homogeneity in annealed pieces of soft steel being nearly perfect. The use of a piezometer of steel in determining the compressibility of mercury up to 6800 kgm. has been described in the paper cited above. The advantages of the steel piezometer have been discussed there, and independent experimental evidence has been presented showing that the compressibility of a piece of mild steel is the same in every direction, and that therefore the piezometer does not change its shape. The results obtained with this method were regular, and in so far justify the use of this material; but further work has led to the conviction that there was present in the method a source of error for which it is hopeless to attempt to calculate the correction. This error is concerned with the leak past the freely moving piston; this leak is less on increasing than on decreasing pressure, so that the previous results are all too small. It seems impossible to determine in what way the error so introduced will vary with the pressure. The total magnitude of the error is probably between 2 and 3 per cent.

---

[8] Carnazzi, Nuov. Cim. (5), 5, 180–189 (1903).

[9] Bridgman, loc. cit.

The method adopted here attempts to keep the advantage of the steel piezometer, while doing away with the uncertainty of the freely moving piston. It was not possible to secure so regular results with the new method as with the old, but on the other hand, any constant source of error seems to be excluded. The method is a modification of one used by Aimé [10] in 1842, and since used in many modified forms by other experimenters. In the original form, the liquid to be investigated was placed in a glass bulb provided with a fine capillary communicating with a vessel containing mercury. The whole affair was then lowered into the sea. Here the increase of pressure forced mercury into the bulb, where it fell to the bottom and remained. On withdrawing from the sea, the maximum volume compression was measured simply by weighing the mercury forced in. Aimé's results were very irregular and incorrect. The most obvious trouble with this method is the tendency of the mercury to collect in drops at the mouth of the capillary. On release of pressure, this drop flows back through the capillary, and the resultant compressibility appears too low. The difficulty may be minimized by making the capillary very small. This is an easy matter when the capillary is made of glass, but when steel is used as here, some special construction must be devised. The form of piezometer adopted is shown in Figure 1. The upper piece B, screws into the shell A. A tight joint between the two is made simply by tightly forcing the narrow edge C on the upper part B into the flat seat at D. It is not desirable to attempt to use any packing material. At the lower part of B there is a very fine channel, E, opening into A. This channel is made by carefully drilling in B a 1/16 inch hole and then plugging the hole with a pin along which a fine scratch has been made. This fine scratch takes the place of the glass capillary when the piezometer is made of glass. It is thus possible to regulate the size of the channel at pleasure. It is a matter of the greatest ease to make such a channel that a pressure of only a few pounds to the square inch will force mercury through it in drops just barely perceptible to the eye, and much too small to be measured by any ordinary balance. In all the work with these piezometers no effect was ever found suggesting in any way the possibility of error introduced by clinging of mercury to the mouth of the channel.

---

[10] Aimé, Ann. de Chim. et Phys., 8, 257–280 (1843).

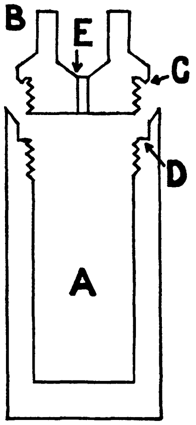

FIGURE 1. The steel piezometer. This is filled with the liquid under investigation and exposed to hydrostatic pressure all over. The pressure forces a measurable quantity of mercury into the chamber A through the fine channel at E, and from this quantity of mercury the change of volume of the liquid originally filling A may be found.

The piezometer may be used in either of two positions, upright or inverted. When used upright, the body A is filled with the liquid to be investigated, water for example, and the cup at B with mercury. The entire piezometer is then placed in a pressure chamber surrounded on all sides by a liquid, to which pressure is applied. This takes the place of lowering into the sea in Aimé's experiment. Mercury flows in through the narrow channel to equalize the pressure within and without, and drops to the bottom. On release of pressure, the water bubbles out through the mercury in B. The piezometer is then unscrewed, the mercury in A weighed, and the total change of volume at the maximum pressure calculated. Into this calculation enter the compressibility of the steel of the piezometer and the compressibility of the mercury. The latter can then be found in terms of the compressibility of water by nearly filling the piezometer with mercury on which floats a little water to fill the piezometer completely. On application of pressure mercury drops through the layer of water, and on release water comes out.

In the inverted position, a sufficient quantity of mercury is placed in the piezometer to cover the bottom, and the fluid with which the piezometer is surrounded in the pressure chamber is chosen the same as that within the piezometer. On the application of pressure, this fluid is forced in, rising through the mercury, and on release the mercury comes out. The quantity of mercury left is weighed, from which the desired change of volume of the fluid is calculated. Here again it is necessary to know the compressibility of the steel of the piezometer and the mercury. The determination of the compressibility of the mercury in the inverted position is as simple as that for finding the compressibility of water in the erect position. The entire piezometer is filled with mercury, and placed inverted in the water by means of which pressure is transmitted. On application of pressure, water bubbles up through the mercury, and on release of pressure, mercury comes out. The compressibility of the water is involved here only as a correction for the volume of the water forced in. In practice, however, it was found desirable to include a little water initially with the mercury, so as to fill completely all the corners. The object of using the piezometer in the inverted position, aside from the check on accuracy afforded by two different arrangements of the apparatus, was to find if possible any effect of the drop clinging to the mouth of the channel. In view of the fact that the surface tension of mercury is greater than that of water, it seemed plausible that the minimum size of a bubble of water that would detach itself from the mouth of the channel and rise through the mercury would be less than the drop of mercury that would fall through water. No such difference could be found, however, in any of the work.

It has been noticed that the method demands the knowledge of two compressibilities besides that of the fluid to be investigated. In the case of mercury these two compressibilities are those of steel and water. The correction for the steel was determined independently by measuring the change of length of a rod under pressure and will be discussed more in detail later in this paper. The effect of the water is small at the low pressures, being simply the change of volume of the slight amount of water forced in, but at higher pressures, where the water may lose as much as 20 per cent in volume, the correction for the change of volume of the water will be 20 per cent for the inverted position and 30 or 40 per cent for the upright position. Given, then, the correction for the steel, it is still necessary to run two sets of determinations to get the compressibility of either water or mercury, and naturally these two determinations give the compressibility of both water and mercury. The data for the water are to be given in a following paper. In calculating the compressibility from these two sets of data, one for the water and the other for mercury, the method of successive approximations was applied. The compressibility of water was first calculated, assuming the compressibility of the mercury to be constant at its initial value at atmospheric pressure. A curve was then plotted giving the volume of water against pressure. From this curve for water, an improved curve for mercury was calculated, from which again a better curve for water was found. In practice it was not necessary to carry the steps further than this.

The relations connecting the compressibility of the water and the mercury with the observed weights of mercury, etc., are given below.

Notation.

V = initial volume of Piezometer,
V_{H_2O} = " " " water,
V_{Hg} = " " " mercury.

Then $V = V_{H_2O} + V_{Hg}$.

Δv_{H_2O} = shrinkage per initial unit vol. of water at pressure under consideration.

Δv_{Hg} = " " " " " " mercury " " " consideration.

Δv_{Fe} = " " " " " " steel " " " consideration;

and in addition:

in the upright position

ΔV_{Hg} = vol. at atmos. pressure of mercury forced in by the pressure in question.

in the inverted position

ΔV_{Hg} = vol. of mercury forced out, etc.

ΔV_{Hg} is the same thing as the volume of the water forced in. The corrected volume of the piezometer at any pressure is evidently V–V.Δv_{Fe}. It is a simple matter to verify the following equations:

Upright position

$$\Delta v_{H_2O} = \frac{\Delta V_{Hg} + V\Delta v_{Fe} - \Delta v_{Hg}\left(\Delta V_{Hg} + V_{Hg}\right)}{V_{H_2O}},$$

$$\Delta v_{Hg} = \frac{\Delta V_{Hg} + V\Delta v_{Fe} - V_{H_2O}\,\Delta v_{H_2O}}{V_{Hg} + \Delta V_{Hg}}.$$

Inverted position

$$\Delta v_{H_2O} = \frac{\Delta V_{Hg} + V \Delta v_{Fe} - V_{Hg} \Delta v_{Hg}}{V_{H_2O} + \Delta V_{Hg}},$$

$$\Delta v_{Hg} = \frac{\Delta V_{Hg} + V \Delta v_{Fe} - \Delta v_{H_2O} (V_{H_2O} + \Delta V_{Hg})}{V_{Hg}}.$$

The following gives a discussion of the minor experimental details that it was necessary to observe.

Considerable care is necessary in filling the piezometer to ensure complete exclusion of air. The procedure in filling was as follows. The piezometer A with the cover B held loosely over it in a suitable frame was placed in a test tube containing distilled water. The test tube was then connected to the air pump and the water boiled under reduced pressure at room temperature, removing the occluded air. The piezometer was then removed from the test tube, the weighed quantity of mercury introduced, and then replaced in the test tube which was again exhausted as before. The mercury had been cleaned with acid and was freshly distilled. Finally, before raising the piezometer above the surface of the water, the cap B was screwed into place with a simple key. Removing from the test tube, the cap B was tightened home by applying a spanner.

This tightening of the cap must be done with especial care, and to irregularities in this most of the irregularities in the data could be traced. Since the piezometer is made of a very mild steel, it is a comparatively easy matter to screw the cap in too far, stripping the thread or shearing off the shoulder. This was avoided by graduating around the top of A, and always screwing B in to the same mark. But even at best, to secure a tight joint, it is necessary to force the cap in pretty tightly, exceeding the elastic limit locally, and thereby introducing probable irregularities as explained before. When the method was first used, a great deal of trouble was found from such irregularities. This was shown most convincingly by the fact that the volume of the piezometer did not remain constant, but changed very slightly after each application of pressure, usually becoming less. This change of volume is not entirely due to the effect of the joint, because it could be mostly removed by annealing. Nevertheless, since the effect of annealing is to remove internal strains, and since internal strains are doubtless introduced at the joint, there is probably some irregular action introduced at the joint. This source of error remains the chief objection to the method, although it can be greatly reduced by proper manipulation. This consists in careful previous annealing, and seasoning by subjecting to pressure several times before the series of measurements is begun. One at least of the previous applications should be to a pressure as high if not higher than that to be reached during the measurements. After treatment like this the piezometers show no further change of volume, and the results with any one are fairly regular. It is a question, however, how good a criterion uniformity of results and permanency of volume are for the uniform compression of the piezometer without change of shape. It must be confessed there seems no valid reason why the piezometer after proper seasoning should not settle down into a steady state in which it gives consistent results with change of shape, and probably it does. The difference of the results with different piezometers is probably to be explained by this effect. The best that can apparently be done is to take the mean of the determinations with several piezometers, all of which individually give consistent results. All of these considerations apply chiefly to determining the compressibility of the incompressible mercury; they have much less weight, and indeed are almost negligible when applied to water.

There is one particular way in which it is very easy to produce irregular results by strains in the piezometer, and one which caused much trouble before the correct explanation was found. If the pressure is pushed too high, the water freezes with sudden decrease of volume. This was not expected when entering on this work, since the freezing curve of water as found by Tammann[11] gives no evidence of the existence of ice above zero. The fact is that there are other forms of ice besides those found by Tammann, one of which is stable at room temperatures. This will be treated in a following paper. The sudden decrease of volume during freezing is accompanied by a rush of liquid through the narrow channel, and, while this rush is taking place, by a momentary excess of pressure outside over that inside. This excess pressure may produce volume set, or if not sufficiently great for that, at least set up internal strains which produce irregularities on subsequent determinations. The irregularities so introduced may be comparatively very high; as much as 10 to 15 per cent in the case of mercury on the next determination. The next value is nearly always too low. The irregularities become smaller with subsequent determinations, but the only satisfactory way is to anneal the piezometer again. Many of the early data had to be discarded because of this freezing effect.

As a consequence of the unforeseen freezing of water at temperatures above zero under high pressure, it is impossible by this method to push the compressibility determinations of mercury to the freezing curve of mercury, as was desired. The difference between the freezing pressure of water and mercury is not very great, comparatively speaking, being about 1500 kgm./cm.^{2} at 15°. By pushing the pressure into the unstable region for water, it is possible to come closer than this to the freezing curve for mercury. At 0° the approach was made to within 700 kgm., and at 22° to within 1000 kgm. Attempts to come closer than this failed. On several occasions the two piezometers, one filled with water and the other with mercury and water, were subjected to pressure simultaneously beyond the freezing pressure of water. The water alone successfully withstood this subcooling, but the water with the mercury always froze. Even when freezing took place, a rough value for the compressibility could be found by using in the calculations the change of volume of the water on freezing. A compressibility for the mercury was thus found lying on a smooth curve with the values at lower pressures, but of course any such procedure as this is questionable. In view of the strong probability that the compressibility of mercury shows no unusual features in the unreached region, it seemed unnecessary to take the measures that would be needed to explore this region, such as the employment of some auxiliary fluid other than water whose freezing point is higher than that of mercury.

---

[11] Tammann, loc. cit., p. 315–344.

It may be mentioned as confirming these views as to the part played by internal strain in making the results irregular, that the irregularity was always much greater after the freezing had taken place after high super-pressures; that is, after the freezing presumably had been most rapid, and the excess pressure on the outside with its resulting deformation greatest.

It will be noticed that the method is essentially an integrating arrangement for measuring the total increase of pressure during the process; that is, at every increase of pressure mercury is forced into the piezometer whether the previous maximum is thereby exceeded or not. In using the method it is essential, therefore, that pressure should be increased continuously to the maximum with no retrogressions. The form of pressure apparatus used made this particularly easy to accomplish. Pressure was produced by a hydraulic ram, the larger piston of which was 6 inches in diameter and the smaller 1 1/8 inches. The 6-inch piston was actuated by the pressure pump of the Société Genevoise, the pressure being run as high as 600 kgm./cm.^{2}.

The motion of the piston was very slow because of the large volumes involved. About 50 strokes of the pump were necessary for an increase of pressure on the high pressure side of 1000 kgm./cm.^{2}. Furthermore, the friction of the packing material, while not very great, retarded greatly the quickness with which the piston moved in response to an increase of pressure. The piston might continue to move for some minutes in response to an increase of pressure on the low-pressure side. The result was that the step-like advance of pressure with each stroke on the low-pressure side was entirely wiped out and converted into a continuous advance on the high-pressure side. The only way in which a retrogression of pressure was likely to occur was by dissipation of the heat of compression. If pressure is rapidly pushed to a maximum, there is produced an increase of temperature. The final equilibrium pressure is lower than the maximum, which corresponds to an unknown temperature. The difficulty was avoided by compressing so slowly that as the pressure approached the maximum the compression was sensibly isothermal. With the apparatus so designed as to reduce the volume of the transmitting fluid to a minimum, it was easy to attain this condition. By comparing results with slower and more rapid compressions a safe rate was found. The maximum pressure of 12,000, for example, could be reached with entire safety in seven or eight minutes. On releasing pressure there was the reverse effect due to cooling, but it is readily seen that there is no error introduced here unless there is actual retrogression of pressure, which is just as easy to avoid as with increasing pressure.

The temperature was kept constant during the compressibility determinations by surrounding the pressure cylinder with a suitable bath, at 0° with ice and water, and at 22° with an electrically regulated thermostat. The piezometers were always submerged for some minutes in this bath before the final adjustments were made. Thus if the compressibility of water were being determined with the piezometer in the upright position, the piezometer was submerged in a test tube of water placed in the bath without the mercury in the upper cup. After temperature equilibrium had been reached, the upper cup was carefully dried with filter paper and the mercury introduced, the lower part still being in the bath. If the piezometer was to be used in the inverted position the procedure was more simple, merely waiting for temperature equilibrium while submerged in the upright position under water or mercury as the case might be. The variations of temperature in the bath at 22° were never more than a few hundredths of a degree. The actual temperature was read with a standardized thermometer.

The volume of the piezometers was found by weighing when full of water at a known temperature and when empty. The filling was performed in the manner above and was more satisfactory than filling with mercury and weighing, since by the use of water it was possible to entirely fill the cracks. The total volume of the piezometers was 1 or 2 cm.^{3} for water and 3 or 4 cm.^{3} for mercury. These small dimensions were necessary to keep the size of the apparatus down within reason, as it was necessary to have the walls of the retaining vessel very heavy in order to withstand the pressures. The cylinder in which the piezometers were placed had a hole 9/16 inches in diameter and was 4 inches on the outside. The small volume of the piezometers places no restriction on the accuracy of the results, however. The weight of the mercury involved in the compression might rise to 3 or 4 gm. for the higher pressures. Weighings were made to 0.0001 gm., so that any error in the weighings is entirely negligible.

Pressure measurements were made with an absolute gauge. This gauge and the various precautions to be observed in its use are described in a previous paper.

Compressibility of the Steel Piezometers.

The experimental determination of the correction for the compressibility of the steel piezometer demands special consideration. The fact must be emphasized that there is no method of determining compressibility in which the compressibility of all the substances concerned can be determined directly, that is, by the application of hydrostatic pressure. There is always a residuum, whatever the method. Thus in the present work, the compressibility of both the water and the mercury involve the compressibility of the steel containing vessels. If an attempt were made to determine by independent experiment the cubic compressibility of the steel, the compressibility of the vessel in which the steel was contained would turn up as a new unknown. The difference of the compressibility of two substances is all that it is possible to get by direct experiment. To get the absolute compressibility of either, the compressibility of the other, the unknown residuum, must be determined by some indirect method. To ensure the greatest accuracy, this residuum should be so chosen as to be as small as possible in comparison with the compressibility in question. Steel, as has been mentioned, is an admirable substance from this point of view.

There are a variety of methods open for the indirect determination of compressibility, all of which depend in some way on the theory of elasticity. A method frequently adopted is to measure two independent elastic constants of a material, such as Young's modulus, or the torsion coefficient, or the bending modulus, and from these to calculate the compressibility by the identical relations of the theory of elasticity. In applying the identical relations, the assumption must be made that the material obeys Hooke's law within the stress range employed, and that it is perfectly homogeneous and isotropic. With these assumptions the identical relations are rigorously exact. The first of these assumptions seems open to but little question. It is the second which is likely to give the most trouble, particularly when the substance experimented on is in the form of hollow tubes, as when the elastic constants have been determined for glass. This method was employed by Amagat [12] and by de Metz,[13] among others.

Another method is to measure the linear compressibilty of the substance in question when subjected to hydrostatic pressure all over and to calculate the cubic compressibility simply by multiplying the linear compressibility by three. This seems preferable to the method of the last paragraph, because the assumptions are reduced to a minimum. The stress, a hydrostatic pressure, is in this method the same during the indirect determination of the cubic compressibility as it is during the actual use of the material in the piezometer. There seems much less chance for complications to be introduced by nonhomogeneity of the material than there is when the compressibility is calculated from two elastic constants, such as Young's modulus and the torsion coefficient. The only assumption made here is that the material is equally compressible in every direction, an assumption which is open to verification by direct experiment. This verification has been made by previous experiments in the paper cited. This method has also been used by several previous experimenters, for example Buchanan,[14] Amagat,[15] and Richards.[16]

In the paper already cited, the linear compressibility of steel was determined at room temperatures up to 6500 kgm./cm.^{2}. These data were inadequate for the present purpose, however, because they did not run to high enough pressures, and the effect of temperature on compressibility was not determined. But the method there used is entirely satisfactory, and new results have since been obtained by it for the purposes of this paper. Briefly, the method consists in enclosing the metal to be experimented on, which is in the form of a rod, in a long steel cylinder, within which it is exposed to the action of hydrostatic pressure all over. The change produced by the pressure in the length of the rod with respect to that of the cylinder is measured by a ring slipping on the rod. The change of length of the cylinder itself is measured directly from the outside.

---

[12] Amagat, C. R., **107**, 618–620 (1888). Ann. de Chim. et Phys. (6), **22**, 95–141 (1891).

[13] De Metz, loc. cit.

[14] Buchanan, Proc. Roy. Soc. Lon., **73**, 296 (1904).

[15] Amagat, C. R., **108**, 727–730, 1889.

[16] Richards, loc. cit.

In the previous work the rod was enclosed in a cylinder of soft tool steel. The maximum pressure, 6500 kgm., was beyond the elastic limit of this steel, so that the material did not remain isotropic. That the elastic limit was exceeded is shown by the considerable hysteresis in the observed elongation of the cylinder. The fact that there is hysteresis suggests that possibly there may be also some slight degree of warping. It was stated in the former paper that the only assumption made in the whole work was in regard to this matter of warping, that is, whether the change of length of the cylinder is the same internally as externally. The effect is probably slight, and in the absence of any plausible way of calculating it was neglected altogether.

Apart from the question of the method used in the present work, and not affecting its validity in the least, there was an error made in the previous paper in the calculations from the data. Correction for this error increases the former value for the compressibility of this steel from 5.30×10^{-7} to 5.59×10^{-7} at 20°. This also will change the value for the compressibility of mercury, as will be explained later.

The tool steel cylinder was not available for the present work, because it would not reach the pressure reached here, 10,000 kgm./cm.^{2}. Another cylinder of nickel steel of the same dimensions as the former one of tool steel was made, therefore, and hardened in oil. With this heat treatment, the elastic limit should be somewhere near 15,000 kgm. The pressure was purposely kept at a low value, never exceeding 10,000 kgm., so as to run no risk of producing set in the inner layers of the cylinder. That no such heterogeneity was introduced is made probable by the fact that the cylinder showed no hysteresis, the relation between extension and pressure being linear both for increasing and decreasing pressure. The former measurements of this extension were made directly with a microscope, reading to 0.001 mm. For this work here, a much more sensitive scheme was used, an adaptation of the Maarten's mirror device so fast coming into general use among engineers. The magnification employed here gave a motion of the scale of 5 cm. for an actual elongation of 0.025 mm. The sensitiveness is, therefore, at least twice that of an interference system, there is also the advantage of great simplicity and steadiness, and best of all, the reading is given directly on a scale, there being no necessity for keeping track of fringes. The Maarten's mirror device disclosed no hysteresis in the elongation of the nickel steel cylinder. The freedom from heterogeneity as shown by the absence of hysteresis makes plausible also the absence of warping, although no direct measurements of this warping were possible.

An attempt was made to show directly the presence of warping by measurements of the change of length of the exterior of the cylinder. Measurements of the extension were made over the middle third and the middle two thirds of the cylinder. Any very large warping might be expected to destroy the proportionality of extension to length, since presumably the warping is confined to the neighborhood of the ends. No such effect could be found, however, within the limits of error which were about 1 per cent.

The argument for the probable absence of warping may be stated as follows. The change of internal length of the cylinder with which we are concerned was measured between two points at each of which the internal diameter of the cylinder undergoes an abrupt change. If the elastic limit of the steel were exceeded, the resulting set and heterogeneity would naturally appear first at these places of sudden change in the dimensions. The effect of heterogeneity at these places would be to produce warping, that is, sections originally plane would no longer remain plane. On the other hand, if the material were never strained beyond the elastic limit, the warping would be negligible. Now the cylinder has been shown by direct experiment to show no hysteresis, and therefore probably not to have been strained beyond the elastic limit. The cylinder, therefore, probably also shows no warping. In any event, one would seem justified in accepting the readings of a cylinder showing no hysteresis in preference to one where the hysteresis might amount to 16 per cent. The effect of warping, whatever it is, can be only slight, since it is itself only a correction on a 5 per cent correction term.

The new determinations made for this work with the nickel steel cylinder were made on the same specimens as those formerly used, which were from the same piece of steel as the piezometers. Determinations were made at two temperatures, 10° and 50°, and up to 10,000 kgm./cm.^{2}. There were only a few changes from the experimental procedure of the previous work. Pressure was measured by measuring the change in the electrical resistance of a coil of manganin wire, instead of a capillary of mercury. This is the pressure gauge that was used in the later work of this paper, and it has been described in detail in a previous paper. The fluid transmitting pressure was usually kerosene instead of the former mixture of water and glycerine. At 10° and at pressure above 8000, the kerosene becomes so viscous that the ring on the test rod no longer slides freely. The great irregularity of the points first obtained was traced to this effect. It may be avoided by using gasolene instead of kerosene at the higher pressures. At 50° the kerosene may be used without trouble over the entire pressure range. The results obtained were not quite so regular as the former results, doubtless because it was impossible to place the cylinder in a position so favorable to the entire removal of all particles of grit after every application of pressure. In this work the cylinder was placed vertically in a thermostat, whereas in the former work it was placed horizontally.

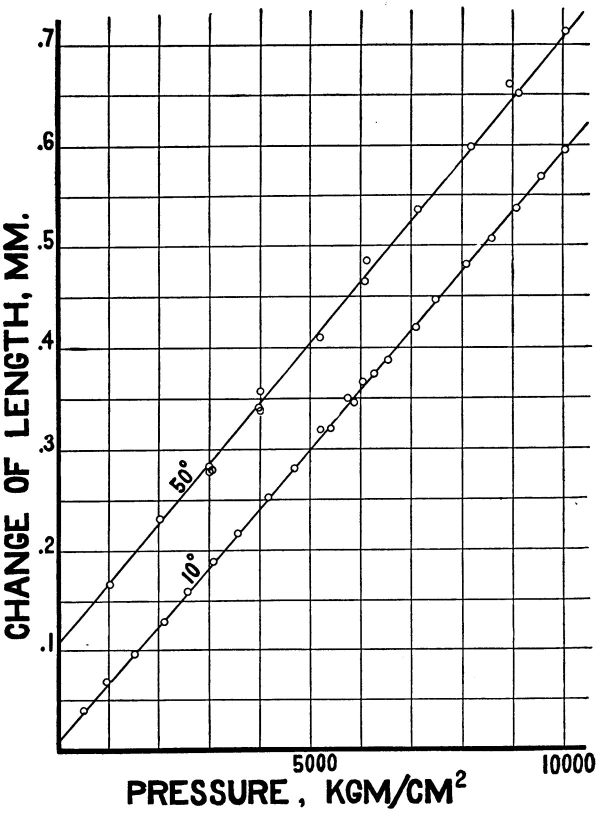

Figure 2. Shows the change of length at two temperatures of a bar of bessemer steel 29.95 cm. long under uniform hydrostatic pressure. The zero reading for each of these temperatures is arbitrary.

The results are shown in Figure 2. The values found for the compressibility were 0.0_6583 at 10° and 0.0_6601 at 50°. The result of the previous determination in the tool steel cylinder at 20° was

0.0_6559. A repetition of the former experiment with the tool steel cylinder gave 0.0_6568 at 20°. It is to be noticed that this value is higher than that previously found, and in the direction toward that shown by the nickel steel cylinder. During the repetition of the experiment the tool steel cylinder also showed less hysteresis than in the early determinations, probably due to the gradual disappearance of the heterogeneity introduced by the previous high pressure during the two and one half years for which the cylinder had been resting. During this last set of determinations the pressure was never raised above 4000 kgm., which is below the elastic limit of the steel.

Whether the true explanation of the discrepancies is to be found in the warping of the cross-section of the cylinder or not, the fact seems to be that when the elastic limit of the material is exceeded there is resulting hysteresis in the elongation, and that this hysteresis is accompanied by low values for the compressibility, the greater the hysteresis, the lower the values. It seems to be justifiable therefore, to accept as most probably correct the values given by this new determination with the nickel steel cylinder. The values given above and the temperature coefficient deduced from them were used in the following computations.

It is to be noticed that the elongation of the nickel steel cylinder under internal pressure, which has appeared in the above as a correction factor, is sufficient to give the cubical compressibility of the nickel steel. This is because, as was pointed out by Mallock[17] in 1904, the elongation of a hollow closed cylinder under internal pressure involves only one elastic constant, the cubic compressibility. This gives for the cubic compressibility 6.2×10^{-7} at 20°. The results are not accurate enough to give the temperature coefficient by this method. The high value of this result compared with that by the direct observation of linear compressibility (62 against 58), is probably due to the difference in the materials, the latter value being for an almost pure iron, while the former is for a nickel-chrome alloy with little or no carbon. (Krupp's trade number for this steel is E. F. 60.0.) It was shown in the previous paper that carbon alone makes very little difference in the result.

This same method, the elongation of a hollow cylinder under internal pressure, has been recently used by Grüneisen[18] in determining the cubic compressibility of various metals at different temperatures. His results for two different specimens of iron at 18° varied from $58. \times 10^{-8}$ to $63. \times 10^{-8}$. The temperature effect on this last specimen was found to be 3.1 × 10^{-8} for 100°, against 1.8 × 10^{-8} for 40° as found above. Grüneisen does not give the temperature coefficient for the iron with the lower compressibility.

---

[17] Mallock, Proc. Roy. Soc. Lon., **74**, 50 (1904).

[18] Grüneisen, Ann. Phys., **33**, 1239–1274 (1910).

In view of the agreement of the results found here with those of Grüneisen, there can seem to be little doubt but that the results found by Richards [19] are affected by some constant error as has been claimed by Grüneisen.[20] The fact that the results here were found by as near an approach to a direct method as possible, that is, by the measurement of the linear compressibility, which also was the method used by Richards, and the fact that these results agree with those of Grüneisen, which were obtained by more indirect methods from the theory of elasticity, would seem to nullify Richards' contention that the results of other observers have been in error because the theory of elasticity gives results 30 per cent out of the way. Richards found for iron 38.5 × 10^{-8} against 58.3 × 10^{-8} above. Since his value for the compressibility of mercury depends directly on his value for the compressibility of iron, the effect of the correction will be to change very appreciably the value for the mercury, as will be mentioned later. The source of error in Richards' work is not entirely clear. He used an electrical method, in which contact was made with a drop of mercury resting on the top of the rod of iron to be measured. Change of shape of this drop of mercury under pressure seems the most likely source of error.

The Data for the Compressibility of Mercury and Calculation of Results.

Determinations were carried out at two temperatures, 0° and 22°. The range is sufficient to give the variation of compressibility with temperature. To get the second temperature derivative of compressibility, observations at several other temperatures would have been necessary, as well as a higher degree of accuracy than was possible to attain in this work. The final values given are the mean of a large number of determinations. At 0°, five different piezometers were used, and over 90 determinations made over the pressure range from 0 to 7000 kgm. At 22°, two piezometers were used, and 38 points determined between 0 and 11,000. The points at 0° were obtained first and show considerable irregularities. As familiarity was gained with the method, and the several sources of error mentioned above became recognized, it was found possible to obtain more regular results. The values at 22° were found after this experience had been gained, and with the two piezometers giving the best results at 0°.

---

[19] Richards, loc. cit.

[20] Grüneisen, Ann. Phys., **25**, 849 (1908).

The points obtained with all five piezometers at 0° are shown in Figure 3, and the points with the best two of these piezometers in Figure 4. The points found with the two piezometers at 22° are shown in Figure 5. The greater regularity of these points is manifest. In both of these figures not all the points actually obtained have been represented, for four or five points, obtained directly after the freezing of the water at too high a pressure, have been discarded.

The data were adjusted and the final values computed in the following way. The work was done independently at each temperature. A straight line was first drawn passing through the assemblage of points. It was not necessary that this line pass through the origin. The deviation of the observed points from the points calculated by the linear formula was then determined. The deviations from this line for each piezometer separately were then plotted on a very much enlarged scale against pressure, and a smooth curve drawn through these deviation points. This deviation curve, together with the fundamental linear equation, gave the best smooth curve connecting change of volume with pressure as determined by each piezometer separately. From these best smooth curves (five at 0°), points were determined at even pressure intervals, 500 or 1000 kgm. apart. At each of these evenly distributed pressures, the weighted

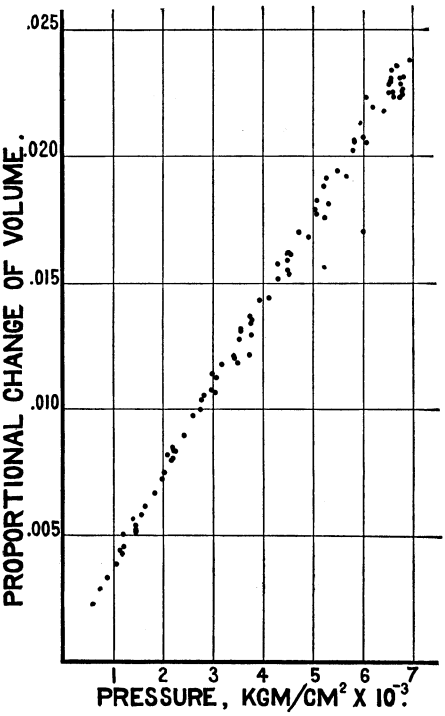

FIGURE 3. Collection of all the results with five piezometers for the compressibility of mercury at 0°.

mean of these five points was taken as the best point at this pressure. Weights were assigned to the smooth curves obtained with each piezometer inversely as the arithmetic difference between the observed deviation points and the smooth deviation curve. The weights at 0°

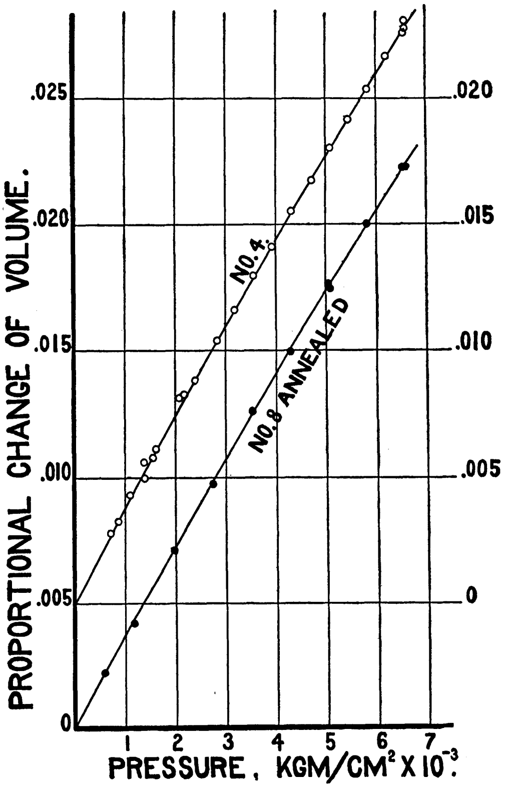

FIGURE 4. The results with the two best piezometers for the compressibility of mercury at 0°. The right-hand vertical scale refers to No. 4, the left-hand scale to No. 8, annealed.

varied from 1 to 7. Finally, a parabola was passed through these best points, the deviations of these weighted best points from the parabola were plotted against pressure, and the smooth curve through these deviations, together with the parabolic formula, was taken as giving the best possible relation between change of volume and pressure.

This was the process used in the final determinations. It has been already explained that the calculation was by means of a method of successive approximations, and that it was necessary to calculate the compressibility of the water as well as that of the mercury. The details of this approximation process have been discussed already in the general discussion of the method. Reference is made to a following paper for the values for the compressibility for water. The procedure in the first steps of the approximation process did not need to be so elaborate as in the above final calculation.

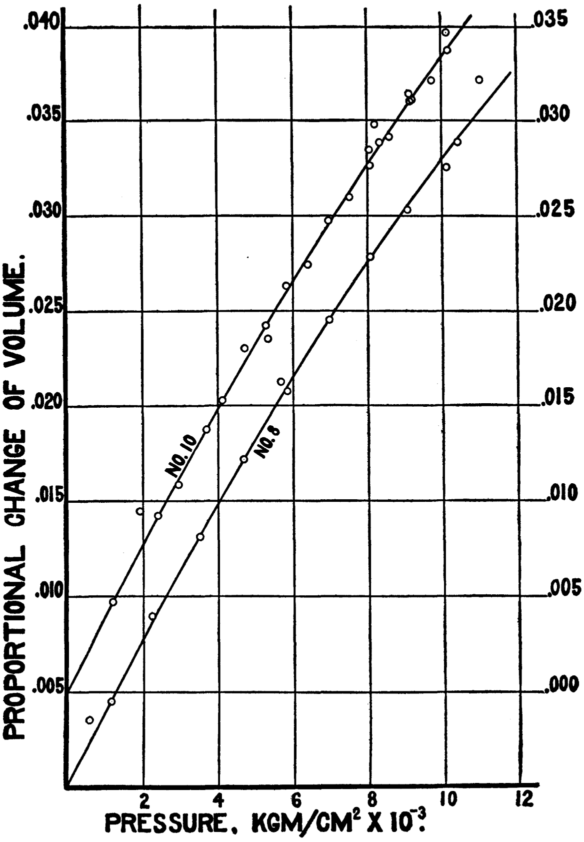

FIGURE 5. The change of volume of liquid mercury at 22° as obtained with two piezometers. The right-hand scale is for No. 10, the left-hand one for No. 8.

The data for 0° and the steps in the final process of adjustment are shown in the tables. Table I. shows the points in the order in which they were determined. The actual computation from the data it is not necessary to show. The formula has already been given by which these computations were made. In Table I., the values for the change

TABLE I.

Data for Compressibility of Hg at 0°.

Piez. No. 4.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Δv_{H_2O} (used in computation).	Δv_{Hg}.
5270	0.1415	0.01913
4520	1290	1621
3750	1147	1370
3000	0991	1142
2220	0796	0847
1450	0578	0538
6050	1527	1709
6770	1617	2283
1000	0414	0337
500	0224	0170
2210	0794	0802
1410	0564	0512
2180	0786	0797
3090	1009	1128
3740	1145	1215
4500	1286	1543
4500	1286	1566
5290	1418	1568
5270	1415	1760
6030	1525	2078
6760	1616	2310

Piez. No. 10.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Δv_{H_2O} (used in computation).	Δv_{Hg}.
1190	0.0485	0.00453
2010	0740	0745
2780	0939	1035
5950	1513	2135
6670	1605	2362
694	0298	0297
3570	1110	1310
4490	1284	1620
5220	1407	1881

Piez. No. 8.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Δv_{H_2O} (used in computation).	Δv_{Hg}.
6810	0.1622	0.02245
6800	1620	2259
6070	1530	2227
5330	1427	1816
4540	1294	1533
3770	1151	1295
3020	0994	1068
2230	0798	0831
1440	0574	0519
1050	0432	0385
1830	0690	0667
2610	0897	0977
3400	1074	1211
4140	1222	1443
4910	1358	1685
5680	1476	1926
6420	1575	2182
6070	1530	2068
4560	1297	1614
3790	1154	1357
2990	0987	1074
6820	1622	2316
6630	1601	2234

Piez. No. 8, annealed

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Δv_{H_2O} (used in computation).	Δv_{Hg}.
6940	0.1636	0.02383
6540	1591	2255
5810	1495	2027
5050	1380	1790
4300	1251	1521
3540	1104	1279
2750	0931	0998
1980	0730	0722

Piez. No. 8 (*cont.*).

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Δv_{H_2O} (used in computation).	Δv_{Hg}.
1170	0.0477	0.00425
595	0259	0224
5090	1387	1771
6600	1598	2259

Piez. No. 11.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Δv_{H_2O} (used in computation).	Δv_{Hg}.
6570	0.1594	0.02298
6200	1547	2197
5450	1442	1941
4720	1325	1704
3940	1184	1434
3180	1028	1179
2400	0844	0896
1620	0631	0617
870	0366	0335
6570	1594	2310
5830	1497	2064
6570	1594	2340
5840	1499	2064
5090	1387	1829
4300	1252	1578
3550	1106	1320
2820	0948	1054
2090	0766	0819
1380	0553	0562
710	0305	0288
1390	0557	0502
2180	0786	0835
1550	0610	0582
1110	0455	0441
2190	0788	0836
6540	1590	2289

of volume of the water, which entered into the computation, are also given, as this effect is rather large. Roughly, the correction introduced by the water was about one third of the total effect due to the change of volume of the mercury. These values for water were taken from the values to be given in greater detail in the following paper.

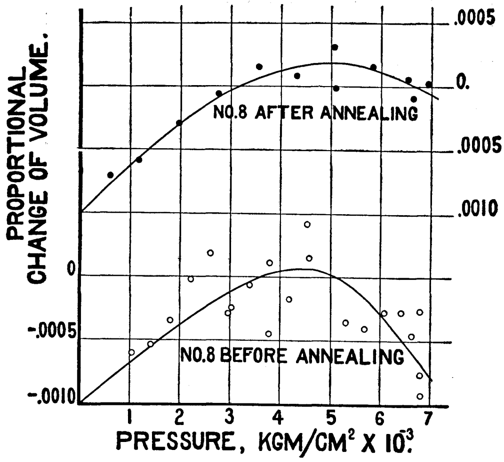

FIGURE 6. The deviations from linearity of the points obtained with one piezometer. This shows the irregularities in the results introduced by internal strains.

Figure 6 gives the deviations of the observed points of two of the sets of readings of Table I. from a straight line. This line, of the form $\Delta V = a + bp$, does not happen to pass through the origin, but gives $\Delta V = 0.001$ at $p = 0$. All the deviation curves, therefore, start from the point $\Delta V = -0.00100$. In Table II. are given the values calculated with the help of the deviation curves for the five piezometers at pressure intervals of 500 kgm., together with the weighted mean of these values. Finally in Table III. are shown the values calculated by the parabolic formula, the weighted experimental values, the deviations, and the finally accepted values, obtained with the smooth deviation curve shown in Figure 7.

The change of volume at any pressure and 0° may be found, either by constructing a curve through the points of Table III., or more accurately by computing at any pressure the change of volume by the formula

$$\Delta v = ap + bp^2,$$

TABLE II.

ADJUSTMENT OF DATA — FINAL VALUES OF COMPRESSIBILITY OF Hg AT 0°.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$	Δv_{Hg} at 0°.						Calculated $\Delta v = ap + bp.^2$	Deviation.	Final value.
	No. 4.	No. 8.	No. 10.	No. 11.	No. 8 annealed.	Weighted mean.			
500	0.00180	0.00180	0.00196	0.00192	0.00187	0.00187	0.00190	−0.00003	0.00189
1000	0362	0361	0389	0385	0369	0372	0376	−4	0374
1500	0549	0543	0569	0577	0553	0560	0561	−1	0559
2000	0737	0721	0753	0763	0731	0739	0741	−2	0739
2500	0921	0899	0931	0945	0909	0917	0919	−2	0918
3000	1100	1070	1110	1120	1086	1096	1094	+2	1095
3500	1272	1246	1285	1292	1259	1269	1267	+2	1269
4000	1442	1414	1458	1458	1428	1437	1436	+1	1439
4500	1606	1576	1630	1628	1596	1605	1602	+3	1605
5000	1777	1735	1795	1793	1761	1770	1767	+3	1769
5500	1923	1889	1955	1954	1934	1929	1927	+2	1929
6000	2073	2039	2111	2111	2084	2085	2085	0	2085
6500	2220	2192	2244	2268	2244	2239	2241	−2	2240
7000	2366	2344	2390	2422	2404	2394	2393	+1	2393
....	4	2.5	1.5	5	10	Weights	....	....	....

Calculated values are by the formula

$$\Delta v = ap + bp^2$$

$$a = 0.0_5 3818$$

$$b = -\log^{-1} 19.7569 - 10$$

TABLE III.

Data for Compressibility of Hg at 22°.

Pressure, kgm./cm.².	Δv_{H_2O} (used in computation).	Δv_{Hg}.
Piez. No. 8.		
4690	0.1258	0.01720
5860	1441	2079
6980	1599	2453
1170	0437	0451
2350	0776	0898
3530	1044	1313
8080	1740	2784
9080	1863	3031
10430	2012	3389
*11640	2128	4101
11030	2070	3720
10130	1980	3257
5690	1416	2129
593	0245	0355
Piez. No. 10.		
10150	0.1982	0.03472
9130	1869	3145
8060	1740	2848
6960	1596	2478
Piez. No. 10 (*cont.*).		
5840	0.1439	0.02132
4720	1264	1806
3570	1052	1378
2410	0787	0923
1210	0450	0472
1930	0657	0947
2950	0918	1087
4140	1160	1530
5350	1364	1855
6410	1521	2243
7520	1670	2599
8600	1806	2916
9740	1938	3218
10180	1985	3377
9150	1872	3106
8080	1766	2765
8200	1756	2984
5290	1355	1926
8290	1767	2887
9210	1878	3113

* Freezes.

where
$$\log a = 4.5819 - 10,$$
$$\log(-b) = 9.7569 - 20,$$

and applying to this computed value the correction given by the deviation curve of Figure 7.

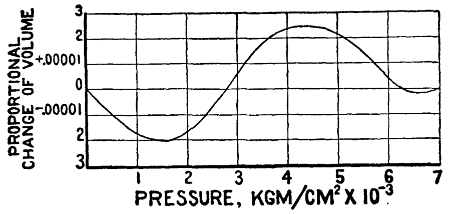

FIGURE 7. The deviation curve for the change of volume at 0°. This is to be used with the formula on page 373.

The data for 22° are shown in a corresponding set of tables and figures. The only difference is that here the parabola was used as the basis for both the first and the final deviation curves. Table IV. corresponds to Table I., Figure 8 to Figure 7, Table V. to Table II., and Table VI. to Table III. The final formula for computation at any pressure is

$$\Delta v = ap + bp^2,$$

where
$$\log a = 4.5911 - 10,$$
$$\log(-b) = 9.7782 - 20,$$

and the final deviation curve from this formula is given in Figure 8.

There are only a few previous determinations of the compressibility of mercury with which these results can be compared, and all of these are at comparatively low pressures, where the percentage accuracy of the above work is naturally less than at the higher pressures. The only way of making the comparison is to find what the compressibility given by the above two expressions would be at atmospheric pressure. The values found in this way from the above data are 0.0_5380 at 0° and 0.0_5395 at 22°.

The early work, done by Regnault,[21] Grassi,[22] Jamin,[23] Amaury et Descamps,[24] and Tait,[25] may be summarily ruled out as too inaccurate for the comparison. The earlier of these determinations were made before the theory of elasticity was well understood, and the work of Jamin, in particular, is a classical instance of how dangerous it is to follow native intuition where the stress and strain system is at all complicated. Jamin's results were 50 per cent too small. Of the more accurate work, Amagat[26] gives 0.0_5379 for the pressure range 0 to 50 kgm., at a temperature apparently unspecified in the original

---

[21] Regnault, Mém. Inst. de France, Six. Mem., **21**, 329–428 (1847).

[22] Grassi, Ann. de Chim. et Phys., **31**, 437–478 (1851).

[23] Jamin, C. R., **66**, 1104–1106 (1868).

[24] Amaury et Descamps, C. R., **68**, 1564–1565 (1869).

[25] Tait, Challenger Report (1889), Phys. and Chem., vol. II, p. 1–76.

TABLE IV.

ADJUSTMENT OF DATA — FINAL VALUES OF COMPRESSIBILITY OF Hg AT 22°.

Pressure. kgm./cm.².	Δv_{Hg} at 22°.			Calculated, $\Delta v = ap + bp^2$.	Deviation.	Final Value.
	No. 8.	No. 10.	Weighted Mean.			
1000	0.00389	0.00389	0.00389	0.00384	+0.00005	0.00389
2000	0766	0766	0766	0756	+10	0766
3000	1129	1131	1130	1116	+14	1130
4000	1482	1485	1483	1465	+18	1483
5000	1818	1823	1820	1800	+20	1820
6000	2141	2149	2144	2124	+20	2144
7000	2451	2461	2454	2436	+18	2454
8000	2746	2761	2751	2736	+15	2751
9000	3026	3044	3030	3024	+06	3030
10000	3290	3313	3297	3300	−03	3297
11000	3540	3568	3549	3564	−15	3549
12000	3776	3809	3787	3816	−29	3787
....	2	1	Wt.	....	....	....

Calculated values are by the formula

$$\Delta v = ap + bp^2$$

$$\log a = 4.5911 - 10$$

$$\log(-b) = 9.7782 - 20$$

---

[26] Amagat, loc. cit.

paper. De Metz,[27] in quoting Amagat, however, gives 0.0_5379 as Amagat's value at 0°. The source from which this knowledge was obtained is not clear. Amagat's results, obtained with seven different piezometers, vary among themselves by 2 per cent. De Metz gives 0.0_5374 at 0° and a pressure range not over 50 kgm., as the mean of results with four piezometers differing among themselves by 5 per cent. De Metz also gives the temperature coefficient of compressibility. This is higher than the value found above, but is such as to bring de Metz's value at 22° up to 0.0_5394, almost identical with the present determination at that temperature. Lately Richards [28] has determined the compressibility to 500 kgm. He gives 0.0_5371 for the pressure range 0–500, at a temperature not specified, probably room temperature. Previous work by Richards, however, had given a value for the temperature coefficient of the mercury the same as that of the glass piezometer. This temperature coefficient is very much smaller than found above, producing a change from 0.0_53710 at 0° to 0.0_53724 at 20°.

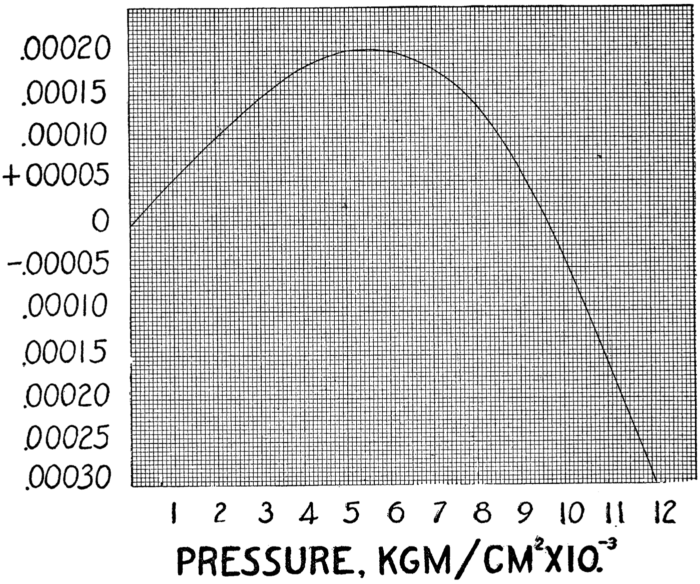

FIGURE 8. The deviation curve for the change of volume at 22°. This is to be used with the formula on page 376.

---

[27] De Metz, loc. cit.

[28] Richards, loc. cit.

It is to be noticed, however, that Richards' value involves directly his own value for the compressibility of iron, which is almost certainly much too low. If the more probable value 0.0_658 is used instead of Richards' value 0.0_638, the value of Richards for mercury becomes 0.0_5391 at room temperature. The change of compressibility with pressure found by Richards is higher than that found above, dropping from 3.80 between 0 and 100 kgm. to 3.60 between 500 and 600 kgm. As mentioned in a previous paper, this is probably due to error in the pressure gauge. Carnazzi[29] has published data over a much wider pressure and temperature range than the other previous observers, up to 3000 kgm., and from 23° to 192°, but with less pretense to accuracy, as only two figures are given in the results. Carnazzi gives 0.0_537 as the initial compressibility at 23°. Since Carnazzi's results are the only ones which give the change of compressibility with pressure over an at all wide pressure range, it may be permitted to anticipate a little in order to compare his results with the present ones. Carnazzi finds a drop in the compressibility of 0.0_64 from 250 kgm. to 2750 kgm. at 23°, against 0.0_625 of the present work. His change in the mean dilatation between 23° and 53° is from 181 at 0 pressure to 157 at 3000, against a change in the mean dilatation between 0° and 22° from 181 to 163 for the same pressures as found in the present work.

Finally, the results may be compared with the results of the previous paper.[30] It has been already stated that the method of the paper was open to question, but it should be remembered, as was stated at the time, that the primary object of that work was to find whether the compressibility of mercury showed any marked change over a pressure range from 0 to 6000, and that the data were obtained because of their bearing on another question. The accuracy was sufficient for the purpose in hand, and the employment of the method seems to have been justified in view of the very much greater speed and ease of manipulation. The initial compressibility at 20°, making correction as already explained for the erroneous value used for the compressibility of steel, was 0.0_5375.

Taken altogether, the agreement with the more accurate of the previous determinations is as satisfactory as could be expected: 380 at 0° against 379 of Amagat and 374 of de Metz, and 395 at 22° against 394 of de Metz and 391 of Richards.

---

[29] Carnazzi, loc. cit.

[30] Bridgman, loc. cit.

Discussion of the Data.

TABLE V.

Volume of Hg at 0° and 22°.

Pressure. kgm./cm.^{2}.	Volume.	
	at 0°.	at 22°.
0	1.00000	1.00398
1000	0.99626	1.00007
2000	99261	0.99627
3000	98905	99264
4000	98561	98909
5000	98231	98571
6000	97914	98246
7000	97607	97934
8000		97637
9000		97356
10000		97088
11000		96835
12000		96596

These data may be used in mapping out the p-v-t surface, and for giving certain information about the thermodynamic behavior of liquid mercury under pressure. The proportional changes of volume given above were calculated in the usual way, by taking the volume under atmospheric pressure and at the temperature in question as the unit volume. To map the p-v-t surface, correction must be made for the change of volume with temperature at atmospheric pressure. Thus, if the volume when $p = 1$ and $t = 0°$ is taken as unity, the values given by the process just mentioned for Δv at 22° must be corrected by multiplying by the ratio of the volume at 22° and $p = 1$ to the volume at 0° and $p = 1$. The actual volume under different pressures, and at 0° and at 22° is given in Table V. In this the value for the total change of volume between 0° and 22° was taken as 0.00398, as given by the most recent work of Callendar and Moss[31] on the expansion of mercury. It appears from their work that the mean coefficient of expansion at 0° is 0.0001805, while the mean coefficient between 0° and 100° is 0.0001817. This gives for $\left(\frac{\partial^2 v}{\partial t^2}\right)_p$ the value 0.0_724, which is evidently beyond the accuracy of this work. That is, for the present purpose, over the temperature and pressure range involved, the isothermals may be assumed to be equally spaced. This is sufficiently accurate at atmospheric pressure, and all our experience with other more compressible liquids would lead us to expect it to be all the more nearly true at higher pressures.

---

[31] Callendar and Moss, Proc. Roy. Soc. Lon., A, 84, 595–597 (1911).

Figure 9 shows the compressibility at these two temperatures and different pressures. The compressibility plotted in Figure 9, is the

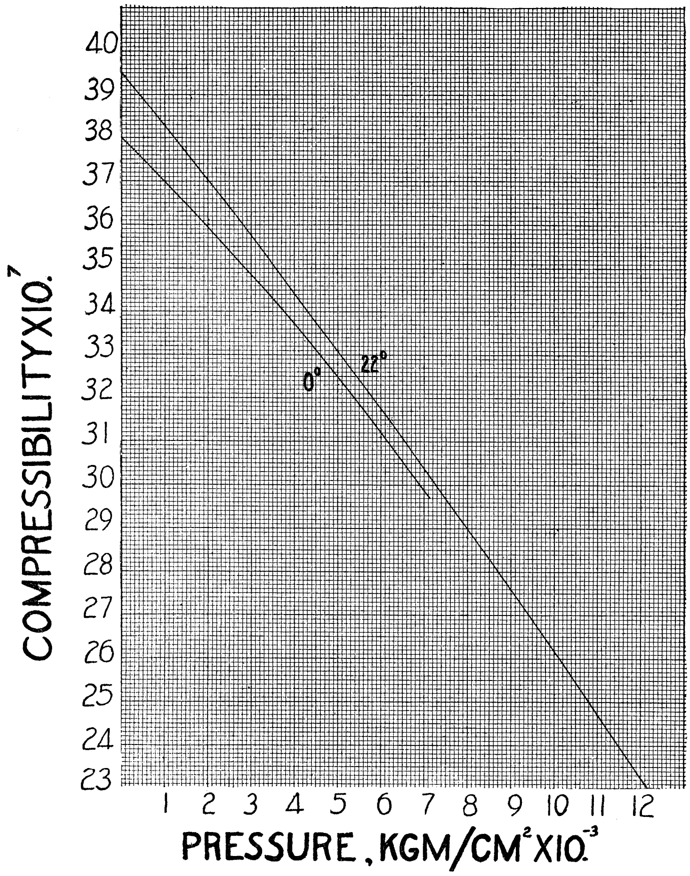

FIGURE 9. The compressibility of mercury at two different temperatures. This compressibility is the instantaneous compressibility $\left(\frac{\partial v}{\partial p}\right)_\tau$.

thermodynamic quantity $\left(\frac{\partial v}{\partial p}\right)_\tau$, which is slightly different from the ordinary meaning of compressibility as used above. It may be obtained at 0° directly from the parabolic formula and the deviation curve. At 22° the results obtained from the parabolic formula and the deviation curve are to be corrected by about 0.4 per cent for the increased initial volume at 22°. The results given in the figure are from smooth curves drawn through the points so determined. The compressibility is less at higher pressures, as it is universally for all liquids, and is greater at higher temperatures, as it is for everything except water. The decrease of compressibility with pressure is very nearly linear, but nevertheless shows a tendency to become more rapid at higher pressures, which is a little surprising. The decrease of compressibility with pressure is more rapid at the higher temperature. Whether the compressibilities at different temperatures would ever become sensibly equal cannot be determined because of the entrance of the solid phase.

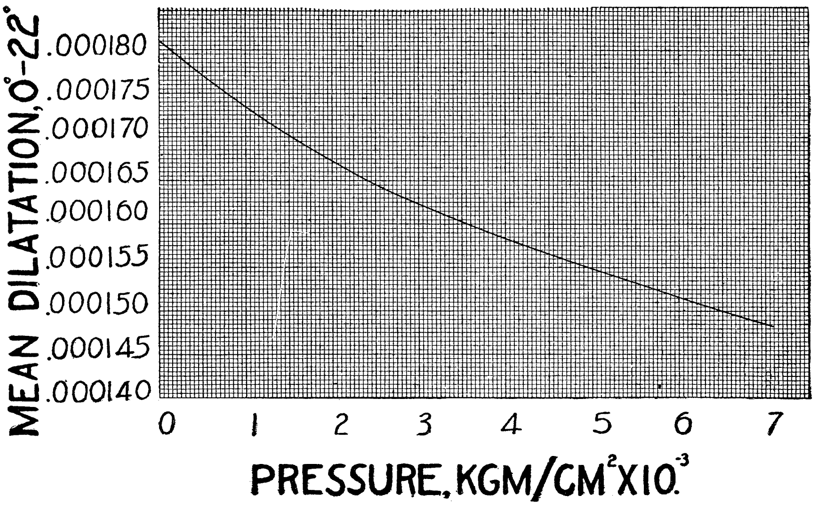

FIGURE 10. The mean dilatation per degree between 0° and 22° for mercury as a function of the pressure.

The dilatation of the mercury, or rather the derivative $\left(\frac{\partial v}{\partial \tau}\right)_p$, may be found from the distance apart of the isothermals at 0° and 22°. The results are shown in Figure 10. The dilatation becomes less at higher pressures, the rate of decrease also becoming less as one would expect.

The data so found, $\left(\frac{\partial v}{\partial \tau}\right)_p$ and $\left(\frac{\partial v}{\partial p}\right)_\tau$, are sufficient to give the difference of the specific heats at different pressures, for we have the relation,

$$C_p - C_v = -\tau \frac{\left(\frac{\partial v}{\partial \tau}\right)_p^2}{\left(\frac{\partial v}{\partial p}\right)_\tau}$$

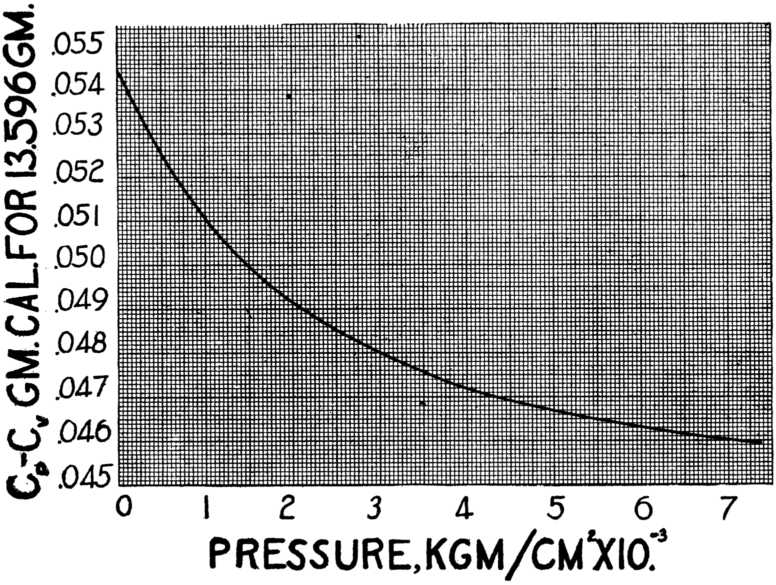

FIGURE 11. The difference of the specific heats as a function of the pressure in gm. cal. for a quantity of mercury occupying 1 cm.^{3} at 0° and atmospheric pressure.

The results in gm. cal. along the isothermal at 0° are given in Figure 11. The difference becomes less at high pressures, the rate of decrease itself decreasing rapidly. The behavior is thus different from that of water, which shows an increase.

The data are not sufficient to give the actual value of either specific heat along the isothermals, but we can find the initial rate of variation from the thermodynamic formula

$$\left(\frac{\partial C_p}{\partial p}\right)_\tau = -\tau\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p.$$

The work of Callendar and Moss[32] gives at atmospheric pressure and 0°

---

[32] Callendar and Moss, loc. cit.

$$-\tau\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p = -273 \times 0.0_7 24$$
$$= -0.0_5 655,$$

C_p being expressed in ergs per cm.^{3} and p in dynes per cm.^{2}. Expressed in gm. cal. and kgm./cm.^{2} this becomes

$$\left(\frac{\partial C_p}{\partial p}\right)_\tau = -0.0_6 154.$$

This variation is so small that we may assume it to remain constant over the pressure range here. This would give a total change of C_p of only 1/4 per cent for 7000 kgm. Probably the change is actually less than this. Table VI. shows the values of C_p calculated with this assumption, and also the values of C_v found from the already calculated values of $C_p - C_v$. It is seen that while C_p decreases with pressure, C_v increases, the increase being more rapid than the decrease. In computing the date of the table, the value of Barnes and Cooke[33] for C_p at atmospheric pressure and 0° was used, 0.03346 gm. cal. per gm., or 0.4549 gm. cal. per cm.^{3}.

TABLE VI.

C_p AND C_v FOR Hg AT 0°.

Pressure. $\frac{\text{kgm.}}{\text{cm.}^2}$.	Specific Heat, gm. cal. for initially Unit Vol. (13.596 gm.)	
	C_p.	C_v.
0	0.4549	0.4003
1000	4547	4035
2000	4546	4056
3000	4544	4063
4000	4543	4073
5000	4541	4073
6000	4540	4077
7000	4538	4079

There are several other quantities of interest that may be deduced from the given data. One of these is the difference between the isothermal and the adiabatic compressibilities. We have the thermodynamic formula

$$\left(\frac{\partial v}{\partial p}\right)_\tau - \left(\frac{\partial v}{\partial p}\right)_\phi = -\frac{\tau}{C_p}\left(\frac{\partial v}{\partial \tau}\right)_p^2.$$

The results are shown in Figure 12. The adiabatic compressibility, therefore, on the isothermal $t = 0°$, decreases less rapidly than the isothermal compressibility.

Intimately connected with the adiabatic compressibility is the temperature effect of compression. For this we have

---

[33] Barnes and Cooke, Phys. Rev., **16**, 65–71 (1903).

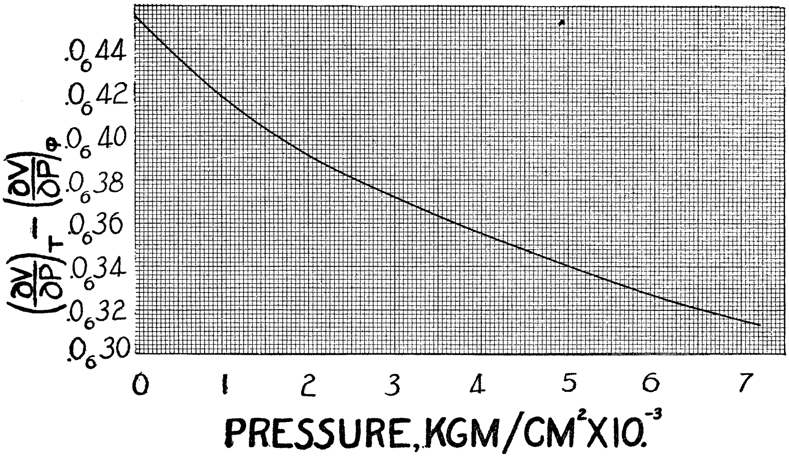

FIGURE 12. The difference between the isothermal and the adiabatic compressibilities as a function of the pressure.

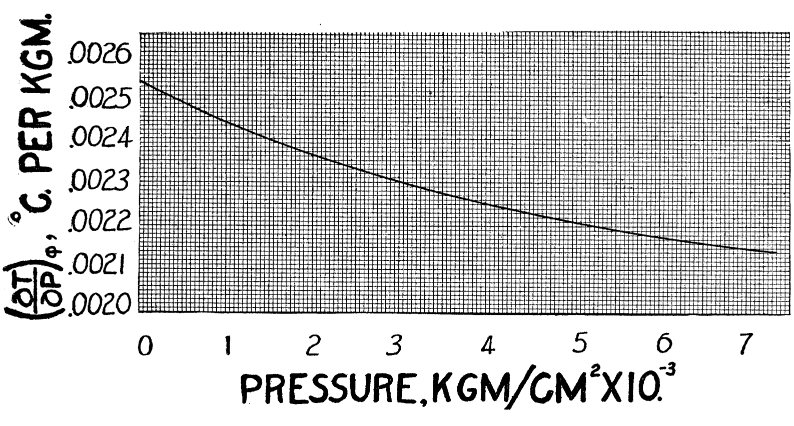

FIGURE 13. The heating effect of compression; that is, the rise of temperature in degrees centigrade for an adiabatic rise of pressure of 1 kgm.

$$\left(\frac{\partial \tau}{\partial p}\right)_\phi = \frac{\tau\left(\frac{\partial v}{\partial \tau}\right)_p}{C_p}.$$

The numerical values of this quantity are shown in Figure 13. The initial rise of temperature is, therefore, about 2°.5 for 1000 kgm. The rise of temperature becomes less at higher pressures, the rate of decrease also decreasing. The rise of temperature for 500 kgm. was found by actual experiment by Richards [34] to be 1°.2, agreeing essentially with above. The fact that this rise of temperature is less at high pressures might at first sight seem surprising, since the work done by the external pressure during a given pressure increase is increasing nearly proportionally to the pressure and the specific heats are nearly constant. It must be, therefore, that most of the work done by external pressure goes toward increasing the internal energy of the liquid, very little being left over to increase the temperature. That this is true is seen at once from the thermodynamic formula

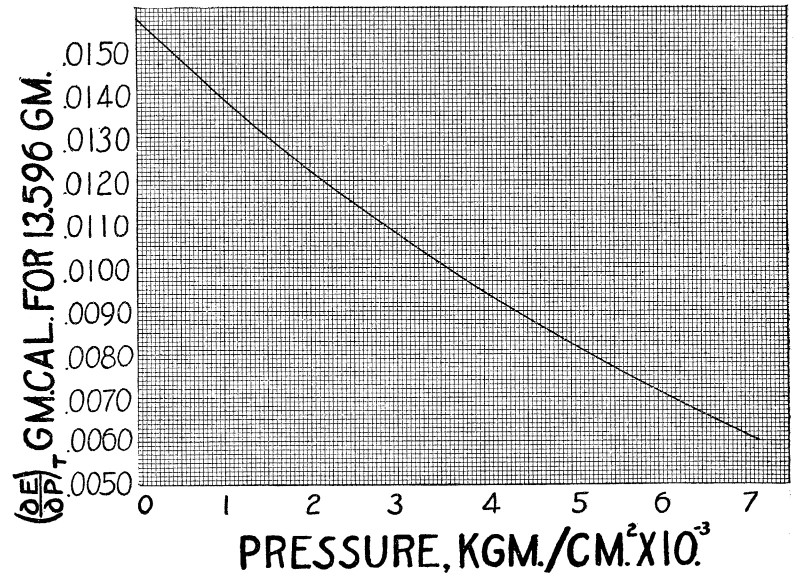

FIGURE 14. The rate of change of internal energy with pressure along an isothermal in gm. cal. for a quantity of mercury occupying 1 cm.^{3} at 0° and atmospheric pressure. Notice that the sign of the derivative is negative.

$$\left(\frac{\partial E}{\partial p}\right)_\phi = -p\left(\frac{\partial v}{\partial p}\right)_\phi,$$

which shows that the internal energy is increasing along an adiabatic, and at a rate very nearly proportional to the pressure. The internal energy decreases along an isothermal, however, as may be inferred from the value of the derivative given by

---

[34] Richards, loc. cit. (1903), p. 40.

$$\left(\frac{\partial E}{\partial p}\right)_\tau = -\left[\tau\left(\frac{\partial v}{\partial \tau}\right)_p + p\left(\frac{\partial v}{\partial p}\right)_\tau\right],$$

and shown in Figure 14. The curvature of Figure 14 is so slight, however, that it seems probable that at a high enough pressure the derivative will vanish and then become positive, so that ultimately the internal energy will increase along an isothermal.

THE CHANGE OF STATE LIQUID–SOLID.

The quantities involved thermodynamically in the passage of a substance from one phase to another at a given pressure and temperature are the change of volume and the latent heat. From these quantities the change of freezing temperature with pressure may be calculated by Clapeyron's equation, $\frac{d\tau}{dp} = \frac{\tau \Delta V}{\Delta H}$. But the experimental difficulties of determining the latent heat are almost prohibitive. This is because in order to withstand high pressures the mass of the steel containing vessel must be much greater than the mass of the substance under experiment. Another method of finding these quantities based on Clapeyron's equation was therefore used, as in practically all the work done previously in this field. If the course of the freezing curve is known, $\frac{d\tau}{dp}$ may be found at any point, which, together with the change of volume at this point and the temperature of transformation, gives the latent heat.

The data were obtained by three methods. The first gives simply the course of the freezing curve. This was found by measuring the electrical resistance at constant temperature as a function of the pressure, freezing being indicated by a sudden drop in the resistance to about one third its value for the liquid. The second method, by far the most important, gives both the melting pressure and the change of volume. It is the same as that used by Tammann,[35] and consists in measuring the volume as a function of the pressure at constant temperature. At the freezing pressure, the volume suddenly changes, so that by plotting volume against pressure, the point of discontinuity gives both the equilibrium pressure and the change of volume. The third method is concerned with a single isolated quantity on the freezing curve, the change of volume on freezing at atmospheric pressure. The existing data were not accurate enough, so this quantity had to be redetermined. The measurements were made by weighing mercury under CS_2, and plotting weight against temperature. Melting is accompanied by a sudden decrease in the displacement and so by a sudden increase in the apparent weight.

---

[35] Tammann, loc. cit., p. 204.

The Freezing Curve by Change of Resistance.

The points on this curve were obtained on two separate occasions; the fall of 1909, and January, 1911, and with two different pieces of apparatus. The data of 1909 are not as accurate as those of 1911, because the gauge was destroyed by an explosion before an entirely satisfactory calibration was made.

The details of the apparatus have been described elsewhere. The absolute gauge, against which the pressure measurements were made directly, has been described in a separate paper. The details of the glass capillary containing the mercury resistance, and the electrical connections with the details of the insulating plug have been described in the paper on the use of mercury as a standard of pressure. The pressure range employed there was only 6800 kgm./cm.^{2}; it has since been found that the same arrangement of apparatus is good to at least 12,000 kgm./cm.^{2}, the range of this paper. The measurements of electrical resistance were made by a null method on a Carey Foster bridge, exactly as in the preceding paper.

One slight change in the details of the measurements as made in 1911 should perhaps be noted, the employment of kerosene as the liquid surrounding the glass capillary instead of a mixture of glycerine and water. This avoids all possibility of short circuiting the terminals of the plug dipping into the mercury cups, and also avoids the necessity for carefully protecting these terminals. A light oil like kerosene is necessary since a heavy oil, such as ordinary lubricating oil, freezes at about 4000 kgm. at room temperature. It was found by independent experiment that at least up to 12,000 kgm. the kerosene does not become so stiff as to refuse to transmit the pressure hydrostatically.

The experimental procedure was the one which would naturally suggest itself, but there are a number of details of manipulation which were necessary to observe. The resistance was measured at appropriate intervals of pressure, the temperature being kept constant. After every increase of pressure it was necessary to wait 10 or 20 minutes for the dissipation of the heat of compression to the surrounding bath, which was kept constant to within 0°.01 with a thermostat. With increasing pressure it was never found possible to reach exactly the freezing pressure, but always the mark was overshot a little. It would have been impossible to land exactly on the mark, in the first place because of the mechanical difficulty of raising the pressure exactly the right amount, in the second place because of the initial effect of heat of compression which would keep the mercury liquid even if the pressure corresponding to the bath temperature were reached, and in the third place, because of the possibility of subcooling the liquid into the region of stability of the solid. With increasing pressure it was always necessary, therefore, to run past the point by from 200 to 400 kgm. Freezing was indicated by a sudden drop in the resistance. This drop was not instantaneous, but might continue for several minutes. Everything points to the spontaneous formation of a crystalline kernal at some point in the capillary, and then the advance of the surface of separation of solid and liquid through the capillary at a rate depending on the amount subcooling, etc.[36] Freezing, when it had once started, usually ran to completion. This was because the volume of the mercury was so small that the change of volume on passing to the solid state was not sufficient to lower the pressure to the equilibrium value. To find the equilibrium pressure, the pressure on the solid phase was lowered until the reaction to the liquid started, and then by rapid work at the pump the pressure was so adjusted that the resistance was in a state of unstable equilibrium, changes of pressure too small to measure on the gauge sufficing to produce a very large increase or decrease of resistance. With a little practice, one could keep the mercury in a partly melted condition for any desired length of time. This was necessary in order to avoid the effect of heat of compression, which might sometimes be so large as to mask the effect sought. The heat of compression of kerosene is so high that it is possible for a decrease of pressure in the kerosene to bring about a freezing of the mercury, the adiabatic drop of temperature with pressure for the kerosene being more rapid than the drop of pressure with temperature on the freezing curve of mercury. To be absolutely certain that there was no such effect the mercury was always kept in the partially melted condition for twenty minutes before recording the equilibrium pressure. To avoid any possibility of error from impurities absorbed by the mercury, pains were taken to find the equilibrium pressure with as little of the solid phase present as possible. This evidently avoids the large depression of the freezing point which would result from the concentration of impurities in the small remaining mass of liquid after the solid had nearly all separated out. The precaution was probably superfluous because the mercury was carefully purified to begin with, and no effect of such a nature was ever detected.

---

[36] To measure the rate of advance of the surface would have been interesting, but to be of value would have demanded some other disposition of apparatus from that used. Evidently the rate of advance of the surface depends more than anything else on the rate at which the heat of transformation is conducted away, which in turn will depend on the size of the glass capillary, and the thermal conductivity of the surrounding liquid. Any results obtained with the apparatus without modification would have had significance only for this piece of apparatus.

One other source of error was guarded against which was especially prominent in the earlier work of 1909. The fluid transmitting pressure from the lower cylinder, in which was the absolute gauge, to the upper cylinder, in which was the mercury, was a thick mixture of either molasses and glycerine or glucose and glycerine. It was necessary to use such a mixture in connection with the absolute gauge in order to avoid leak at the high pressures. But there is the disadvantage that the viscosity of either of these fluids increases so rapidly with pressure that high pressures are not transmitted immediately through the connecting pipe from the lower to the upper cylinder. This connecting pipe was 15 inches long and 1/16 inch internal diameter. That the pressure was transmitted slowly was shown by the fact that after pressure had been increased in the lower cylinder by advancing the piston, the absolute gauge in the lower cylinder indicated a fall of pressure for some minutes, while the change of mercury resistance in the upper cylinder indicated a corresponding rise, evidently due to the slow flow of liquid from the lower to the upper cylinder. The effect was troublesome only at the higher pressures, the pressure coefficient of the effect being very high, and was very much greater for the mixture of glycerine and molasses used in 1909 than for the glycerine and glucose of 1911. In the extreme case, glycerine and molasses at 12,000 kgm., it was necessary to wait two hours for the equalization of pressure. For most of the pressures used the effect disappeared more rapidly than the heat of compression. To avoid error from this effect, the decrease of resistance indicating freezing must come after an increase of pressure in the lower cylinder, and the converse increase of resistance after a decrease of pressure. The measurements were made with this in mind.

The temperature measurements above zero were made with a Tonnelot thermometer calibrated at the Bureau of Weights and Measures in Paris. Below zero the readings of 1911 were made with a toluol thermometer calibrated at the Reichsanstalt, and in 1909 with a mercury thermometer made by Green of New York, the zero correction for which was the only correction applied. In any case, the errors in the temperature readings were less than the possible error in the pressure. The temperature was kept constant with an ordinary thermostatic device; a stream of ice water, or for the lower temperatures a stream of $CaCl_2$ brine, running constantly into the bath, which was automatically heated with a Simplex heating coil when the temperature fell too low. The temperature did not vary more than 0°.01 during a run, whereas a change of 0°.05 is necessary to produce a change in the equilibrium pressure of 10 kgm. which was about the limit of accuracy of the gauge. The temperature range of the experiment was from —15° to +20°. Since the freezing curve as determined between +20° and —15° extra-

TABLE VII.

Freezing Pressure at Different Temperatures by the Method of Change of Electrical Resistance. Data of 1909.

Temp. °C.	Equilibrium Pressure, kgm. /cm.².		Difference, kgm./ cm.².
	Observed.	Calculated.	
+14.35	10720	10600	+120
+21.0	11860	11910	− 50
+16.8	10850	11060	−210
+10.06	9620	9730	−110
+16.25	11010	10960	+ 50
+ 4.04	8540	8530	+ 10
0.00	7730	7730	0
0.00	7730	7730	0
− 8.52	6060	6040	+ 20
−15.09	4730	4730	0
+ 9.68	9690	9660	+ 30
+21.42	12070	11990	+ 80

Calculated values by the formula

$$p = a(t + 38.85)$$

where $a = \frac{7730}{38.85} = 198.9$

polates almost linearly to the ordinary freezing point at —38°.8 and atmospheric pressure, it was not thought necessary to make the special effort demanded to run a thermostat at temperatures below —15°.

One other remote possibility of error was guarded against. The capillaries containing the mercury were fine, the bore being about 0.1 mm. It was thought barely possible that the curvature of the surface might be sufficient to produce a rise of internal pressure in the mercury sufficient to change slightly the external pressure required to hold liquid and solid in equilibrium. This effect was shown to be negligible by using two capillaries of different sizes, one three times the diameter of the other. The equilibrium pressure found at 0° with the larger capillary was 7680 kgm., and with the smaller 7660. The divergence is in the direction to be expected, but it is of the same order as the experimental discrepancies. The data of 1911 were ob-

TABLE VIII.

Freezing Pressure of Mercury at Different Temperatures by the Method of Change of Electrical Resistance. Data of 1911.

Temp. °C.	Equilibrium Pressure. kgm./cm.².		Difference kgm./cm.².
	Observed.	Calculated.	
4.95	8570	8660	−90
9.92	9640	9640	0
14.86	10600	10620	−20
19.98	11640	11630	+10
0.00	7680	7680	0
−14.40	4790	4830	−40
−9.70	5630	5760	−130
0.00	7660	7680	−20

Calculated values by the formula

$$p = a(t + 38^\circ.85)$$

where

$$a = \frac{7680}{38.85} = 197.7$$

tained with the larger of the above mentioned capillaries; those of 1909 with one of intermediate size.

The actual data follow. Those for 1909 are in Table VII. and in Figure 15. The data are given in the order in which they were collected. The two determinations at the higher pressures after the run with regularly decreasing pressures were made, the one at 9°.68 to correct the obviously bad point determined first of all, and the one at 21°.4 to make sure that there had been no systematic error introduced after the regular decrease of pressure of the first points. In addition, the three points determined during the initial testing of the apparatus, before the thermostat was installed, are given at the very end. The temperature error here easily accounts for the discrepancies of these last three points. As was stated before, the gauge with which these determinations were made was destroyed before it could be satisfactorily calibrated. The data used in the reduction of the gauge readings were simply the measured dimensions of the gauge, which could not be determined with the requisite accuracy. The column showing the calculated pressure must be taken, therefore, as merely evidence showing the regularity of the results and slight departure from linearity, and not as giving accurately the absolute pressures.

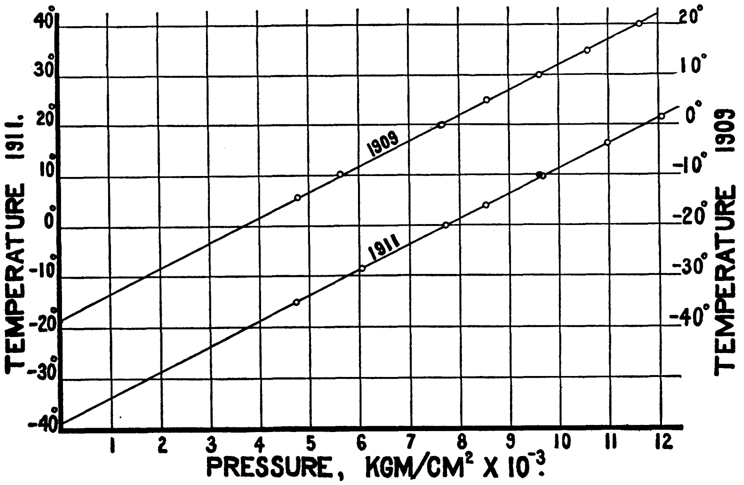

FIGURE 15. The melting curve of mercury by the change of resistance method.

Table VIII. and Figure 15 give the results of 1911. The method by which the results were calculated was the same combination of numerical computation with graphical construction already used in finding the compressibility. A straight line was passed through the point at 9640 and 9°.92, and the departure of the observed pressure values from those calculated by the linear relation plotted on a large scale. A smooth curve was then drawn through the midst of these points, and the final values calculated by applying to the smooth values the small correction determined from the smooth curve.

The points of 1911, except for the two bad ones mentioned above, lie on a smooth curve within the possible errors in reading the gauge. The departure from linearity, although slight, is pronounced in the direction of concavity toward the pressure axis, that is, less rapid rise of freezing temperature at the higher pressures.

There seems no reason why the points of 1909 are not just as valuable in indicating the manner of departure from linearity as those of 1911, since all the pressure readings are affected alike by the incomplete calibration of the gauge. The error in the gauge readings of 1909 is simply due to inaccurate knowledge of the cross-section. The following correction was applied, therefore, to the gauge constant of 1909. The best straight line through the points of 1911 was determined (graphically from the smooth correction curve) and also that through the points of 1909. The former gives a change of pressure of 197.1 kgm./cm.^{2} per degree rise of temperature ; the latter 199.2. The observed pressures of 1909 were all reduced in the ratio of 197.1 to 199.2. A smooth curve was then passed through these corrected values by the method described above. Finally, to determine the most probable departure of the freezing curve from linearity, the mean of the two correction curves, those for the data of 1909 and 1911, was taken. These curves differ nowhere by more than the possible errors in reading the pressure gauge. From this curve it is possible to find immediately the tangent to the melting curve at the origin.

Finally, all these results may be collected into the following form. At any given temperature the melting pressure is to be found by adding to the pressure given by the formula $p = 196.5\ (t + 38.85)$ the small correction term given graphically in Figure 16. The initial rise of pressure per degree rise of the freezing point is therefore 196.5 kgm./cm.^{2}; at 12,000 kgm. this has become only 1/2 per cent greater, so slight is the departure from linearity. The value of the initial slope, 196.5, has no more certainty than the single series of observations of 1911, but the departure from linearity shown in Figure 16 has the greater weight which should be given to the mean of two independent series of observations with different apparatus.

A number of data collected incidentally in the course of the work may be mentioned here, because they throw some light on certain properties of mercury under pressure, even if these are not the thermodynamic properties which are the particular subject of this paper.

The electrical resistance of the liquid mercury was usually measured over the entire range up to the freezing pressure. The matter of the electrical resistance of mercury under pressure has already been treated in a paper in which the pressure range was only 6800 kgm./cm.². The results obtained during the present work were pretty irregular, discrepancies of 1 or 2 per cent not being rare; but within the limits of error, the empirical formula given in the previous paper may be used by extrapolation up to the freezing pressure, at least within the present temperature range from — 15° to + 20°. The irregularities observed in the present work were without doubt due to the strains set up in the glass by the passage of the mercury from one state to the other. To reach the accuracy of which the measurements are susceptible it would be necessary to repeat the above resistance measurements, taking care never to push the pressure beyond the freezing value.

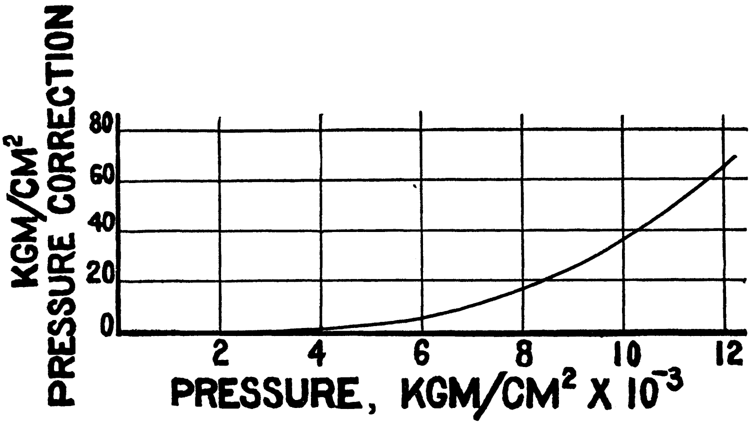

FIGURE 16. Departure of the melting curve of mercury from linearity. The initial slope is 196.5 kgm. for a rise of temperature of 1° C.

The electrical resistance of the solid mercury was also usually measured. These results cannot be expected to much more than indicate the order of the effect, for in addition to the comparatively small irregularities mentioned above, as due to elastic after-effects and hysteresis, comparatively large temporary alterations in the glass capillary are probably produced by the freezing of the mercury. The results are given in Table IX. *R* is the resistance of the mercury reduced by taking as unity the resistance of the liquid at atmospheric pressure and the corresponding temperature. *R* for the liquid was obtained by extrapolating beyond the freezing point to the pressure at which the resistance of the solid was measured. The resistance of the solid shows a distinct tendency to become less at the higher pressures and temperatures. The effect of temperature only would be to raise the resistance. The pressure coefficient of resistance must be negative, therefore, as for all other pure metals, and must have a value at least such that 200 kgm. increase of pressure produces a greater fall of resistance than 1° rise of temperature produces rise of resistance. This means that the pressure coefficient of the solid is greater than 0.0004/200 = 0.000002. The table also makes evident the tendency of the change of resistance liquid-solid to become less at higher pressures and temperatures. This indicates that the effect of pressure on the resistance of the liquid is greater than the effect on the solid, as one would expect, although the reverse is true for the temperature effect. This enables an upper limit to be placed on the pressure coefficient of the solid, since the coefficient of the liquid is known. This upper limit is about ten times the lower limit set above. It hardly seems worth while to at-

TABLE IX.

CHANGE OF ELECTRICAL RESISTANCE WHEN MERCURY CHANGES FROM THE LIQUID TO THE SOLID AT VARIOUS PRESSURES.

Temp. °C.	Pressure, kgm./cm.².		Resistance in Terms of Resistance at Atmos. Pressure and Temp. of the Measurement.			
	Pressure on the Solid.	Freezing Pressure.	Solid.	Liquid.	Change.	Ratio.
16.2	10960	10870	0.211	0.761	0.550	3.61
14.3	10660	10490	247	764	517	3.09
10.0	9960	9640	234	777	543	3.48
4.0	9220	8450	251	791	540	3.15
0.0	7660	7650	264	817	553	3.09
0.0	7610	7650	241	816	575	3.39
−15.1	5450	4680	258	863	605	3.35

tempt to force the above very imperfect data to give more accurate results.

It may be mentioned, however, that the above results are fully as consistent as the results which have been obtained by previous observers for the electrical resistance of solid mercury at atmospheric pressure. Thus Weber[37] found the following values for the ratio of the conductivity of the solid mercury to that of the liquid out of which it is freezing : 3.2, 4.2, 3.9, 4.0, 3.5, 4.0. Taking the reciprocals so as to compare with the above form, these become 0.31, 0.24, 0.26, 0.29, 0.25 ; different measurements of the same quantity. Cailletet and Bouty[38] give the single number 0.24, while Grunmach in his first paper[39] gives 0.67 and redetermines it in a later paper[40] as 0.40. The high values of Grunmach are doubtless to be explained by the formation of cracks in the mercury when freezing. This error can hardly come in the present work. In explanation of the other outstanding discrepancies, the fact does not seem to have been sufficiently considered that mercury freezes into crystals which may have different conductivities in different directions. It is known that the conductivity of bismuth, for example, may change by 60 per cent in different directions, and that of iron glance by 100 per cent. It is to be expected, therefore, that the particular form of vessel in which the mercury is frozen, by influencing the position in which the crystals tend to separate out, would have an effect on the apparent change of resistance on freezing.[41]

Finally, mention may be made of an unsuccessful attempt to get the heat of transformation from these same resistance measurements. The idea was to measure the depression of the freezing point occasioned by dissolving some metallic impurity in the mercury, the commencing of freezing being indicated by a kink in the curve giving resistance as a function of the pressure. The depression of the freezing point gives the heat of transformation by a well known formula. The difficulty with the method is that there is no metal which gives a depression of the freezing point sufficiently large to give the desired accuracy. Few metals depress the freezing point at all, and those which do show a eutectic point 1° or 2° below the normal. In a preliminary testing out of this idea, the resistance of a 5 per cent Cd amalgam was measured at 21°.5. Beginning at between 1000 and 2000 kgm. the pressure coefficient was found abnormally large over the pressure range up to and including 12,000 kgm., which is the freezing pressure of pure mercury at 21°.5. The time required in reaching equilibrium was also abnormally long. Both these facts indicate the separating out of some component from the amalgam. Between 12,000 and 13,000, this process of separation seemed to have been completed, and from 13,000 to 13,500 the behaviour was entirely normal. The explanation is simple. The effect of pressure is to raise the entire melting diagram Hg—Cd, the Hg end more than the Cd end. (See Figure 17.) This raising is presumably accompanied by a shifting of the proportions of the two metals present in the eutectic mixture. The initial temperature and proportion of the two metals present in the amalgam may be represented by the point A (in this case $t = 21°.5$ and $x = 5$ per cent), but when the pressure has risen sufficiently to bring the melting curve up to A, with further rise of pressure A slides along the rising curve, always at con-

---

[37] Weber, Wied. Ann., **25**, 245–252 (1885), and **36**, 587–591 (1888).

[38] Cailletet et Bouty, C. R., **100**, 1188 (1885).

[39] Grunmach, Wied. Ann., **35**, 764–772 (1888).

[40] Grunmach, Wied. Ann., **37**, 508–515 (1889).

[41] Since the writing of this paper Onnes (Kon. Akad. Wet. Proc., **4**, 113–115 (1911)) has given data from which the ratio of the resistance of solid to liquid mercury may be found to be 0.237. This value was computed by the author from the values given in Science Abstracts for the resistance of a given quantity of mercury (172.7 ohms at 0°C., and 39.7 ohms in the solid state at the melting temperature).

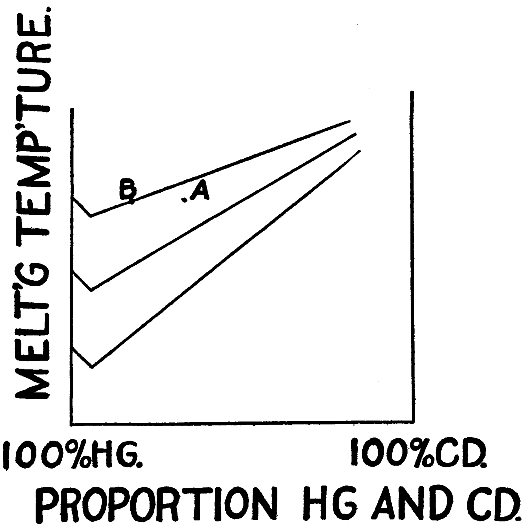

FIGURE 17. Showing the raising of the melting curve of mixtures of mercury and cadmium with increasing pressure.

stant temperature, shown by the point B on the highest melting curve of the diagram, until the eutectic point is reached, where complete solidification sets in. This takes place at a pressure slightly higher than the normal freezing pressure for the pure mercury, as shown experimentally above, but the precise amount will depend on the unknown way in which the proportions of the eutectic mixture have changed. To obtain the data desired by this method, A must initially lie to the left of the eutectic point corresponding to the particular freezing pressure instead of to the right, as in the diagram. The results evidently cannot be accurate, and it was therefore not thought worth while to push the investigation further at this time, particularly since the destruction of the gauge mentioned before came as the direct result of the high pressure reached above. An investigation of the change of eutectic proportions under pressure would make an interesting research for its own sake.

The Equilibrium Data by the Change of Volume Method.

The method was essentially that of Tammann, and gives both the change of volume and the pressure at a given temperature. It consists in measuring the displacement of the piston by which pressure is produced as a function of the pressure. Freezing is indicated by an interruption of the regular rise of pressure with advance of the piston. It is at once obvious that an absolute essential for the success of the method, and at the same time the hardest condition to maintain under high pressures, is the entire freedom from leak of the moving piston and the other parts of the apparatus. Tammann found this trouble at pressures above 2000 kgm./cm.^{2}, and avoided it in part by using a very heavy oil for transmitting pressure. In this present work a new packing device was adopted which secured entire freedom from leak even with so thin a fluid as kerosene or mercury. Data will be given in support of this.

The data needed at any point in addition to the equilibrium pressure and temperature are the amount of the advance of the piston during constant pressure, the quantity of liquid involved in the change, and the cross-section of the advancing piston. The first two may evidently be measured directly, but the last changes with pressure by an amount not susceptible to direct measurement. Here, as in all pressure measurements, the distortion of the containing vessel enters as a disturbing factor. But it should be pointed out that here the effect of the distortion is a minimum. It has been quite impossible up to the present to make direct determinations of compressibility, for example, by this method, because the changes of volume of the liquid are accompanied by unknown changes of volume of the same order in the containing vessel. But here, where the changes take place at constant pressure, the vessel remains constant during the change, and the only distortion which need be taken into account at all is the change of area of the cylinder, a change which is easy to calculate, and which furthermore never in the present work rose above 2 per cent of the total effect. To make this matter clearer, take the example of water. A pressure sufficient to change the volume of water by 20 per cent might introduce a change of about 2 per cent in the volume of the very heavy cylinders of this present work. This change of 2 per cent takes no account of the change of volume introduced by the compression of the packing of the various connecting pipes, etc., which are necessary if the pressure is to be measured at all accurately. This change due to the tightening of the packing is evidently incalculable, but may presumably be as large as the other effect. The change of volume as indicated by the advance of the piston is affected, therefore, by a quantity which may very reasonably be supposed to be 4 per cent on 20 per cent, that is, 1/5 of the total effect measured. Compare this with the change of volume during freezing at constant pressure. Here the change of volume of the rest of the vessel and the packing plays no part whatever, the only correction is 2 per cent for the change in cross-section of the cylinder. That is, a correction of 2 per cent which may be approximately determined, against a wholly unknown correction of 20 per cent. It should be remarked, however, that if once the compressibility of the water has been determined in some other way, it may be used in an apparatus of this form to determine the unknown distortion, and so the compressibility of other liquids may be determined.

Description of Apparatus.

The apparatus consisted essentially of two cylinders, connected by a piece of very heavy nickel steel tubing 12 inches long. The upper cylinder was placed in a hydraulic press, and the pressure was produced in this by a piston forced down by the ram of the press. The amount of motion of the piston was measured with a micrometer screw reading to 0.0001 inch. There were no valves in any part of the apparatus, as it is difficult to make these capable of withstanding high pressures. The apparatus was initially filled entirely full of liquid after the air had been exhausted with an air pump, and the piston was then introduced into the upper cylinder. The dimensions of the various parts were chosen so that the maximum pressure desired could be obtained with a single stroke. This upper cylinder was freely exposed to the air of the room, with no special device to keep the temperature at any definite value.

The lower cylinder contained the mercury, the subject of the experiment, and was surrounded by a bath kept at constant temperature by a thermostat. The mercury was contained in a cylindrical steel shell fitting loosely the hole in the cylinder. The same kerosene which entirely filled all other parts of the apparatus and transmitted pressure from the upper to the lower cylinder also entirely surrounded the walls of the shell containing the mercury. This arrangement was necessary, because if the mercury had been allowed to come in contact with the walls of the cylinder, the steel would have become amalgamated, and the cylinder speedily ruptured. Whereas, the steel shell in which the mercury was contained being surrounded on the outside by kerosene, and so being subjected to a purely hydrostatic pressure equal all over, experienced no amalgamation whatever.[42]

Screwed into the bottom of this lower cylinder, directly immersed in the kerosene and so subjected to the same pressure as the mercury, was an insulating plug carrying a coil of manganin wire with which the pressure was measured.

The procedure was as follows : After filling the apparatus with kerosene, the thermostat was raised around it and adjusted to the temperature desired. When a steady state was reached, the resistance of the manganin coil was read on the Carey Foster bridge, thus giving the pressure zero. The piston was then introduced into the upper cylinder, and pressure increased to a value a few hundred atmospheres short of the freezing pressure at the temperature of the thermostat. After pressure equilibrium had been attained by dissipation of the heat of compression, the pressure was read from the resistance of the manganin coil and the position of the piston was read with the micrometer. Two readings of the resistance of the manganin were made corresponding to the two positions of the eight-point switch of the Carey Foster bridge. These readings were made before and after reading the position of the piston. Since the circuits were non-inductive, the bridge could be used with the galvanometer circuit permanently closed. These two readings are, therefore, really two independent readings of the pressure, and agreement between them is indicative of the attainment of pressure equilibrium. It was not necessary to take any such precautions in measuring the position of the piston, for the friction of the packing prevented all motion after the initial increase of pressure.

---

[42] See These Proceedings, No. 14, 1911, for a discussion of the amalgamation of steel under high pressures.

The above procedure, reading of pressure and piston position, was repeated at appropriate pressure intervals up to several hundred or perhaps a thousand kgm. beyond the freezing pressure. On plotting piston displacement against pressure, the freezing is shown by a discontinuity in the curve. Similar readings were also made on release of pressure, and so another value for the change of volume found. On releasing pressure the discontinuity is more sudden than with increasing pressure, because it is impossible to superheat the crystalline solid on decreasing pressure, but the liquid may be subcooled on increasing pressure. Because of this, and for another reason to be explained later connected with the distortion of the steel, the value found with decreasing pressure was without exception accepted as the correct value.

In the use of this apparatus and in the calculation of the data, there are numerous corrections or disturbing factors which will now be considered in detail.

Leak. — As already stated, the most obvious and apparently the greatest difficulty with the method, particularly at high pressures, is the question of leak. It might perhaps be possible to correct for this as was done sometimes by Tammann by weighing the quantity of liquid escaping past the piston in a given time, but this correction would always be unsatisfactory in cases where, as here, the total motion of the piston during freezing is small (0.2 inch) and many extend over an hour or more. It has been stated that there was absolutely no leak. This was proved by the fact that the piston and upper end of the packing, when removed from the cylinder after the end of an experiment, were always perfectly dry, even though the total time over which pressure has been applied might reach into several days, as it did on several occasions. That there was no leak in any other part of the apparatus was proved by the self-consistency of the results as well as by special experiment. On one occasion pressure was left at 7500 over night, temperature being kept constant with a bath of ice and water, and in the morning had not dropped by as much as the smallest amount perceptible with the manganin resistance, namely 2 kgm./cm.^{2}.

The effect of leak, if there were one, would be to make the values of Δv during increase larger, and during decrease smaller. The values did actually in the great majority of cases disagree in this way. That this was not due to leak will be evident from a discussion of

Elastic After-Effects. — In the ordinary sense of the word, elastic after-effects, as is indicated by the name, are purely elastic phenomena, complete recovery after any application of stress always occurring, provided time enough is allowed. There are also other effects of somewhat the same general character, such as hysteresis, not usually included in the name. But there will be included in this discussion any effect in virtue of which the strain is not a single valued function of the stress only. The general nature and interpretation of these effects is still obscure, but there are a few facts which are well known. For instance, in all ordinary testing of materials it is first necessary to accommodate the metal to the particular stress conditions of the moment. The strain under a given stress is not the same the first time the stress is applied as the second, and not until the application of the stress a number of times does the strain come to depend always in the same way on the stress. Even after complete accommodation has been attained, the material may continue to show elastic after-effects, that is, continued yield after the application, or continued recovery after the release or stress. Or it may also show hysteresis. These effects become increasingly important as the magnitude of the stress is increased, or as the character of the stress changes from one uniform throughout the mass to one changing from point to point. The effects become most important of all when the material itself has become non-homogeneous by the exceeding of the elastic limit in some places while the remaining parts are without permanent deformation.

Various effects of just this kind are to be expected in these experiments, and may perhaps be fairly large in comparison with the usual magnitude of the effects, because of the wide range of stress here employed. It should be pointed out that one advantage of this method, namely, that the elastic deformation of the vessels does not enter the results, is in part offset by the various effects of the kind mentioned here, because in virtue of them the volume of the containing vessel may change while freezing or melting is going on at constant pressure. Furthermore, these effects, which are themselves intrinsically small, may appear with magnified effect in the result. Thus the actual change of volume of the mercury during freezing is about 1 per cent of the total internal volume of the containing vessel, so that a change of volume of 1/100 per cent of the containing vessel produced by elastic after-effects during freezing will appear in the result magnified to 1 per cent. As a matter of fact, there were found discrepancies between the values under increasing and decreasing pressure amounting in the worst case to 3 per cent.

It was possible, however, by an examination of the discrepancies themselves and by a brief consideration of the method of experiment to select from these the most probably accurate results. During the course of an experiment, the stress history of the steel in its bearing on this effect was as follows. Pressure was pushed to a value somewhat short of the freezing pressure, the readings were made, and then pressure increased again, etc., until the subcooled region had been entered far enough for freezing to begin. This first stage might occupy an hour. The second stage was that of approximately constant pressure during freezing, which might require from an hour to an hour and a half. During the third stage, pressure was increased a few hundred atmospheres beyond the freezing pressure, held at the maximum for a while, and then decreased to the melting point again. This occupied another hour. The fourth stage, melting at constant pressure, ran more rapidly than freezing, but might consume an hour. Finally a few readings below the freezing pressure, rarely more than half an hour. It is to be noticed that during melting the pressure has been held in the immediate neighborhood of the maximum for some hours, and that this melting pressure is only slightly removed from the maximum, whereas during freezing, the stress has just been increased over nearly the entire range and the time for accommodation has been much shorter. All our experience with elastic after-effects would lead us to predict that during melting these effects would be very much less important than during freezing. We would furthermore predict that the change of volume found during freezing would be greater than that during melting, for the piston must advance to compensate for the increasing volume of the steel vessels as well as for the decreased volume of the mercury.

These conclusions were verified by the data. The values found during melting were always self-consistent, lying on a smooth curve, and could be repeated. But those found during freezing might vary wildly within the 3 per cent limit mentioned above. Furthermore, the inconsistent results were always larger than the consistent ones, provided that the procedure was as described above. There seemed to be no connection between the duration of the pressure and the amount of the discrepancy.

We already have evidence enough to make it extremely probable that the discrepancy was not due to leak, although it is of the right sign. But the fact that the discrepancy is reversed in sign so as to indicate a leak in instead of a leak out, if the stress is applied differently from above, renders certain the conclusion that the effect is not due to a leak. The succession of points on the melting curve, the procedure in getting one of which was described above, was in general obtained by starting at low temperatures and pressures and working up to the higher values. Each maximum pressure, then, was higher than the preceding maximum. But if the preceding maximum was higher than the following one, the discrepancy was reversed in sign, the values during freezing being too low, while those during melting still lay on the same smooth curve as before. This certainly cannot be due to leak. Neither is it in accord with the general nature of other elastic after-effects at low pressures. But other experience of this same general nature at these high pressures indicates that this is probably the general nature of the effect at high pressures. It is as if the subsequent application of pressure, and possibly the change of temperature also, changes somewhat the position of the molecules, like shaking a magnet, so that they become free again to resume their natural elastic recovery from the previous greater maximum. One experiment with a hollow steel cylinder subjected to external hydrostatic pressure strikingly suggested the same general explanation. This cylinder had been previously subjected to a pressure many times beyond the elastic limit, so that the metal had flowed toward the center, decreasing the internal volume. On removing the pressure there was some slight elastic recovery of the internal volume, but not nearly as much as was to be expected. But the next increase of external pressure produced in the initial stages a very marked increase of internal volume, instead of a decrease, the natural effect of the pressure. It must be that in some way the pressure loosened up the molecules so that they were free to resume their natural recovery.

Other slight differences suggest also that these discrepancies are of the general nature of elastic after-effects. Because of breakage, several different pieces of apparatus were used. The discrepancy was always greatest with the thickest-walled vessels. It has been observed several times in other connections that elastic after-effects are greater with the greater mass of metal, because this allows greater heterogeneity of strain and greater volume in which to store the effect, with consequent longer time of recovery. At a given pressure the effect in a new piece of apparatus was smaller before it had been subjected to the greatest maximum than it was at this same pressure after being so subjected to the maximum. In general, the effect was likely to increase with time, showing fatigue of the metal. In one case, in the similar measurements on water, to be described elsewhere, rupture of the vessel was foreshadowed by an increase of the effect beyond 3 per cent.

There may be some slight effect of permanent set mixed up with the above effects. An undoubted set was always very distinctly obvious after the first application of the greatest maximum. This application was usually made in a preliminary test in order to season the apparatus before the measurements were undertaken. This applies particularly to those three or four occasions after the lower cylinder had been broken. The seasoning of the upper cylinder was done more carefully, and is described elsewhere. The set must have been nearly all removed by this seasoning, but any subsequent set would still affect only those results for increasing pressure.

In view of all these considerations, the course actually adopted seems justified; namely, to retain only those values found during melting, that is, during decreasing pressure. In consequence, in some two or three of these last determinations, and in many of those on water, the experimental determination with increasing pressure was entirely omitted.

Elastic Deformation. — It has already been stated that the only way in which elastic deformation, that is, a deformation depending only on the pressure, enters, is in the correction for the change of cross-section of the upper cylinder. Although the value finally adopted for this correction is small, only 1.3 per cent at 10,000 kgm /cm.^{2}, still it must be admitted that the greatest uncertainty in the work is precisely in determining this correction. The difficulty comes because of the very high pressure employed, which renders doubtful the calculation by the ordinary theory of elasticity. If the maximum pressure used in the experiment, 12,000 kgm., were the greatest pressure involved, the case would not be so doubtful, because the elastic limit of the steel is not greatly exceeded here. Indeed, if it were possible to harden the steel uniformly throughout its mass, reaching to a depth of 1 1/2 inches, the elastic limit would not be reached until about 15,000 kgm., and there would not be much question in applying the ordinary equations of elasticity. But it is impossible to raise the elastic limit throughout the metal by quenching, and the interior of the cylinder always shows some set at 12,000. Since the accuracy of the whole method depends on accurate knowledge of the cross-section it was necessary to remove every vestige of set in this part of the apparatus. This was done by subjecting the cylinder initially for five or six hours to a pressure of 24,000 kgm. This was sufficient to stretch the inside of the cylinder from its initial value of 1/2 inch to nearly 9/16 inch. The cylinder was then reamed out to 9/16 inch for its entire length, and this was the form in which it was finally used. The effectiveness of the treatment is shown by the fact that the cylinder has shown no further change of so much as 0.0001 inch on the internal diameter.

The present condition of the cylinder is therefore far from one of a state of ease; there are certainly internal strains. But it should be noticed that this fact in itself is not sufficient to destroy the applicability of the equations of elasticity. Provided only that the metal shows no further set after the first application, and that strain remains proportional to stress, any stress will produce the same additional strain as the same stress applied from a state of ease. The long interval of time for which the maximum pressure was exerted, and the large excess of this pressure over any subsequent pressure, make it exceedingly probable that such a state has actually been reached. The residual stress in the cylinder is then of exactly the same nature as the stress in a gun with shrunk-on hoops, and the deformation may be calculated by the ordinary theory. It may be mentioned, in support of this position, that measurements have been made of the external elastic deformation of another such cylinder of the same steel up to 10,000 kgm., showing agreement with the accepted theory to at least 5 per cent, with no trace of hysteresis.

The calculation of the actual deformation of the cylinder according to the elastic theory would be impossible because of the indeterminate nature of the boundary conditions. An approximate solution only can be obtained, in which the end effects are neglected altogether. This solution is nevertheless probably accurate enough, because the end effect in other similar cases in which the rigorous solution is known has been shown to be negligible. It is well to remember in considering the validity of these approximations that the maximum value of the correction at the highest pressure is only 1.6 per cent.

The internal diameter of the cylinder does not expand uniformly under pressure. The expansion may be supposed to have its greatest value at points removed from the position of the piston by at most a few diameters. The expansion throughout the greater length of the cylinder is constant, therefore, and equal to the value it would have in a cylinder infinitely long and of the same radial dimensions. But for a short distance beyond the head of the piston the expansion varies from its maximum value to a value which may be shown to become half this maximum at the piston itself. Now if we suppose that the cylinder is so long that as the piston moves at constant pressure (during freezing or melting) the locality of transition in dimensions travels bodily with the piston, then a moment's consideration shows that the volume swept out by the piston is equal to the length of stroke multiplied by the area of the cylinder at its locality of maximum distortion. The assumption does not seem forced in view of the fact that the length of the cylinder is between ten and fifteen diameters.

The formula for the displacement under these conditions may be found in any book on elasticity. We have

$$\Delta b = \frac{bP}{a^2 - b^2}\left(\frac{a^2}{2\mu} + \frac{2b^2}{3\kappa} \cdot \frac{4\mu + 3\kappa}{12\mu}\right),$$

where b is the internal and a the external radius, μ the shearing modulus, and κ the compressibility modulus.

a was measured directly from the outside of the cylinder and was 3.536 cm.; b was found from a measurement of the plug at the end of the piston after this plug had been forced to conform to the hole by the application of high pressure. It has been already stated that no change in b could be detected during the course of the experiments of so much as 0.00004 cm. b was found to be 0.7183 cm. μ and κ were found by the ordinary equations of elasticity from Young's modulus, taken as 2×10^6 kgm./cm.^{2}, and Poisson's ratio, taken as 0.28. These quantities vary only slightly in different grades of steel. The values of μ and κ calculated in this way were found to be 7.81×10^5 and 15.2×10^5 respectively. Substituting in the formula gives directly

$$\Delta b = 0.00491 \text{ cm. for } 10{,}000 \text{ kgm./cm.}^2.$$

Whence the change of area, $\Delta A = \dfrac{2 \times 0.00491}{.7183}$

$$= 1.35 \text{ per cent for } 10{,}000 \text{ kgm./cm.}^2.$$

Temperature Corrections. — There are a variety of temperature corrections to be considered; those which are to be met in any physical measurement, and those which were peculiar to this particular work. The ordinary corrections concern only the reading of the temperatures and may be dismissed with a few words. Temperature about the lower cylinder was maintained constant to 0°.01 with a thermostat. Above zero this temperature was read with a Tonnelot thermometer calibrated at the Bureau of Weights and Measures in Paris. The correction for the zero was determined, but it was not necessary to apply any of the other corrections. Readings on this are probably accurate to 0°.01. Below zero, readings were made on a toluol thermometer, graduated to 0°.1, and calibrated at the Reichsanstalt. In addition to the corrections of the Reichsanstalt, the zero correction was applied. This is accurate to 0°.1, which corresponds to the accuracy of the pressure measurements.

Of the corrections peculiar to this work, the temperature effect on the pressure readings was the simplest. The manganin resistance coil with which pressure was measured was placed in the lower cylinder with the mercury, and so was exposed to the same changes of temperature. It has already been shown in the paper on the gauge, that within the temperature limits of this work the pressure coefficient of resistance is constant. The only temperature effect is on the total resistance of the coil, which, therefore, merely displaces the zero. This zero was usually redetermined directly at every temperature, but in a few cases where it was inconvenient to release the pressure to zero between two sets of readings at different temperatures a calculated correction was applied. This correction was determined from an independent measurement of the temperature coefficient of the zero of one of the four manganin coils with which pressure was measured. These four coils were made from contiguous pieces of the same piece of wire. The greatest change of the zero from this effect amounts to 400 kgm. between — 20° and 0°. Above zero the correction becomes very much smaller, as this particular kind of manganin shows a maximum resistance at 28°. It will be noticed that it was necessary to keep the bath temperature constant to only 0°.5, in order to remain within the errors of the pressure readings.

By far the most serious correction is due to the fact that the lower cylinder with the mercury under experiment is at one temperature, while the upper cylinder where the measurements of the change of volume are made is at another temperature, the temperature of the room. It is readily seen that the change of volume during melting, for example, as measured by the displacement of the piston of the upper cylinder, will be in error by the expansion at constant pressure of the liquid kerosene on passing from the temperature of the lower to that of the upper cylinder. This error has the same sign during both melting and freezing. The change of volume so measured will be too large if the lower cylinder is colder than the upper, and too small in the reverse case. The correction evidently becomes rapidly larger with the increase in the difference of temperature, but because thermal dilatation becomes less with increasing pressure, this correction fortunately becomes smaller at high pressures, where it is harder to determine. The maximum value for the correction in this work was 2 per cent over the range + 20° to — 20°.

This correction seems to have been entirely overlooked by Tammann. It might very possibly amount at the maximum to over 10 per cent for temperature ranges over 100° such as he employed. The effect of the correction will not be to change at all his co-ordinates of the melting curve, but might possibly modify somewhat the way in which Δv apparently tends toward zero at high temperatures and pressures. This latter point has some theoretical significance in Tammann's theory of solid-liquid.

The correction had to be determined by direct experiment, as there were no data by which it could be calculated. The discussion, which is somewhat long and involved, will be given in the following separate section.

The Thermal Dilatation of Kerosene at Constant Pressure.

Since the accuracy desired was not very high, the maximum value of the correction being 2 per cent, a procedure was adopted which was rapid, but not accurate enough to employ in determining this quantity as a physical constant interesting in itself. The method consisted essentially in filling the entire apparatus with kerosene, lower as well as upper cylinder, immersing the lower cylinder in the constant temperature bath, and plotting piston displacement against pressure. Then the lower cylinder was allowed to come to room temperature, and again the piston displacement and the corresponding pressures noted. The difference of displacement at the two temperatures gives the change of volume of the kerosene which was in the lower cylinder on expanding from the one temperature to the other. It is to be noticed that this gives the thermal dilatation of a quantity of kerosene of unknown mass but of known volume. To find the dilatation as ordinarily defined, we should require the compressibility, so that we might know the original volume of the kerosene which at the given pressure completely filled the lower cylinder. But the data as given by the experiment are exactly the data needed in making the correction. For suppose the change of volume of the mercury on melting at a certain temperature and pressure is approximately 1 cm.^{3}. We require to know how much this 1 cm.^{3} of displaced kerosene has changed in volume on passing from one temperature to another at constant pressure, and we are not interested at all in the original volume of this 1 cm.^{3} of kerosene.

The procedure as roughly outlined above is evidently liable to a multitude of errors. It is exactly similar to the corresponding method of obtaining compressibilities against which objections were made in the introduction. But it is to be said in extenuation that the correction is small, and that the maximum correction comes at the low pressure where the objections of the introduction have little weight. The correction at $-20°$ of 2 per cent corresponds to only 3500 kgm. At this pressure and with a cylinder seasoned by exposing to 24,000 kgm. there need be no hesitation even in applying the method to accurate determinations of the compressibility. The correction at 0° and 7500 kgm. has already dropped to 0.6 per cent.

The corrections to apply in determining this maximum correction of 2 per cent are the corrections on the volume of the lower cylinder brought about by the changes in temperature and pressure. The volume was found by weighing the lower cylinder when full of mercury. To be subtracted from this volume was the volume of a copper block inserted to reduce to manageableness the total quantity of the kerosene, and the volume of the manganin pressure gauge. The volume occupied by the kerosene increases with pressure both because of the stretching of the cylinder and the shrinking of the copper and the manganin gauge. The stretching of the cylinder was calculated by the theory of elasticity as outlined above. A slight modification of the formula is necessary because the cylinder carries the end thrust of the pressure. The total correction for the stretching of the cylinder is 1.4 per cent at 10,000 kgm. The effect of the copper and the small quantity of mica washers in the insulating plug were assumed to be represented by the compressibility 0.0_51, the compressibility of the copper alone being 0.0_69. This correction amounts to 0.5 per cent at 10,000. Together, the two effects produce a total change on the effective volume of kerosene of 1.00 cm.^{3} per 10,000 kgm., on an initial volume of 28.6 cm.^{3}. The correction for the thermal dilatation of the lower cylinder was found from the known dilatation of steel at ordinary pressures, assuming it to be independent of pressure.

In making the actual measurements, endeavor was made to avoid as far as possible the small effect of mechanical hysteresis. The set of readings at —15°, for example, was obtained as follows. The piston displacement was measured with increase of pressure from 3500 to 5800 kgm. with the lower cylinder at +20°; the lower cylinder was then cooled to —15°, and the displacement measured from 5800 back to 3500; and finally the lower cylinder was warmed again to +20° and the displacement measured from 3500 to 5800. The difference between the second curve and the mean of the first and the third, which differed only very slightly, gives at any one pressure the expansion of the corresponding amount of kerosene on passing from —15° to +20°, since the temperature of the upper cylinder was also +20°. This difference was found for a number of pressures for the range 3500 to 5800, and a smooth curve drawn through these differences. From this curve was taken the difference corresponding to the freezing pressure of mercury at —15°. This process was performed for four temperatures, —20°, 15°, —7°, and 0°, and four points were thus determined on the correction curve. It was not necessary to obtain other points above 0° on the curve, because the correction was already small at 0° and the other end of the curve is fixed by definition as passing through the value zero at 20°. Through these five points, —20° to 20°, another smooth curve was drawn, giving at any temperature the piston displacement when the amount of kerosene in the lower cylinder passes from that temperature to +20° at the pressure corresponding to the freezing pressure of mercury at that temperature. Finally this curve gave the required percentage correction curve by translating piston displacements into volumes and dividing by the volume of the kerosene in the lower cylinder at the corresponding pressure as already determined. The correction curve actually used is shown in Figure 18. It is obtained by combining with this temperature correction the correction already determined for the elastic deformation of the upper cylinder.

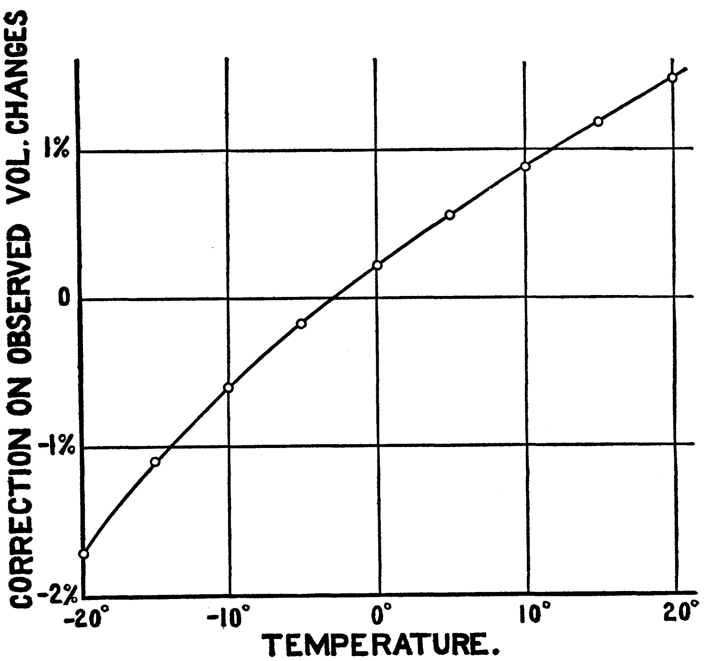

Figure 18. The corrections due to the thermal dilatation of the transmitting liquid and the elastic deformation of the cylinder to be applied to the directly measured change of liquid mercury when it passes to the solid state.

The correction curve so determined is not linear, the values being 2.0 per cent at —20°, 0.65 per cent at 0°, and 0 at +20°. The departure from linearity is evidently due to the decreasing dilatation of the kerosene under high pressures.

Temperature Correction for the Upper Cylinder. — In the form of apparatus used in this experiment there is one other small correction because the upper cylinder is exposed to the slightly varying room temperature. If the room temperature changes during freezing, the observed change of volume is evidently incorrect by the thermal expansion at the particular pressure of the total quantity of kerosene in the upper cylinder. The temperature changes were usually very slight. They were made still smaller at the cylinder itself by enveloping this in a large mass of cotton batting. The temperature of the cylinder was read with a thermometer directly in contact with it. The correction demands an approximate knowledge of the quantity of kerosene in the upper cylinder, which was obtained by measurement of the position of the piston. The thermal dilatation of the kerosene at any given temperature was found from the correction curve already described, making the justifiable assumption that at constant pressure the dilatation is sensibly constant over the temperature range. The maximum correction was at —20°, where the dilatation is a maximum, and where the temperature variation, 0°.7, happened also to be a maximum. The correction here was 0.5 per cent. Above 10° the correction was entirely negligible.

Possible Change of State of the Transmitting Liquid. — The effect of any freezing of the kerosene with contraction during the freezing of the mercury would be to make the change of volume appear too large. This possibility was entirely eliminated, however, incidentally by the measurements determining the thermal dilatation of the kerosene. At any given temperature these measurements extended considerably beyond the freezing pressure of the mercury, and no evidence of a change of state with change of volume was found.

Measurements of the Piston Displacement.—These measurements were made with a Brown and Sharpe micrometer reading to 0.0001 inches. The measurements were made between a point on the head of the advancing ram which drives the piston and a fixed point on the frame of the press against which the cylinder is pressed. There are two possibilities of error here. One, the most serious, is warping of the entire frame of the press. Such an effect was detected and may give rise to discrepancies of 0.002 inch over the entire stroke of 4 inches. It was obviated by making four measurements of every displacement between four pairs of points at the four corners of the frame of the press. The second error may come from elastic deformation of the parts of the press between the head of the ram and the fixed point on the frame, so that the measured change of length does not give the actual piston displacement. The effect, which is in any event small, was obviated by taking advantage of the fact that there is considerable friction in the packings. In virtue of this it is possible to vary the pressure on the low pressure end of the ram over a considerable range without producing motion of the piston, and so without altering the high pressure. Now it is the pressure on the low pressure end which produces distortion in the frame of the press, the cylinder at the high pressure end taking up in itself the effects of the high pressure. The effect of distortion in the frame was avoided, therefore, by adjusting the low pressure before every measurement of displacement to the same constant value for all values of the high pressure in the immediate neighborhood of the freezing point.

The Pressure Measurements. — The method of measuring these high pressures, with a discussion of the various sources of error has been given in another paper. Briefly, the pressures were obtained from the measured change of resistance of a coil of manganin wire immersed directly in the kerosene of the pressure chamber which contained the mercury under investigation. The coils, four of which were used during this investigation, were each calibrated separately against an absolute gauge. These were capable of reproducing the gauge with as much accuracy as the gauge itself could be read, which was about 8 kgm./cm.^{2}.

THE DATA.

The actual determinations by this method extended over about two months, from Oct. 13 to Dec. 3, 1910. In all, eleven points were determined, from $-20°$ to $+18°$, both with increasing and decreasing pressure. The measurements were sandwiched in between similar ones on water which are to be described in another paper. The apparatus was taken apart and set up a great number of times, both in the course of the ordinary manipulations attending the experiment and in making those changes necessary because of the piecemeal explosion of various parts of the apparatus. There were at least five such explosions during the experiment; two lower cylinders being burst, two upper cylinders, and one connecting pipe. The accuracy of the work is spoken for by the fact that determinations with all these different groupings of apparatus, including change of the pressure measuring coils, gave points lying on the same curve. This does not appear so strikingly from the actual data given, but it must be remembered that by far the greater number of measurements during this time were made on water, where the same independence of the particular piece of apparatus is also shown. The first five measurements on mercury were made with different combinations of apparatus; the last six were made with the same set up. The equilibrium pressures found in all eleven sets of readings are equally worthy of acceptance, but the volume measurements of the first five must be discarded because the effect of changes of room temperature was not sufficiently recognized at the time, and no correction was applied for it. The data of the same period for water, however, where the total change of volume is larger and the correction of less account, give consistent values for the change of volume also.

First for the equilibrium pressure. This was ordinarily found at only two points, one with increasing and the other with decreasing pressure, but in order to make sure that this equilibrium pressure was a perfectly definite quantity, independent of the quantity of mercury melted, equilibrium was found, during the first two or three runs, with various proportions of the solid melted. This is shown in Figure 19 (Oct. 13), where the piston displacement is plotted against pressure. The vertical part of the curve shows the period of transition. The equilibrium pressure thus appears to be the same whether the freezing is nearly complete or only just begun. It is possible to get much

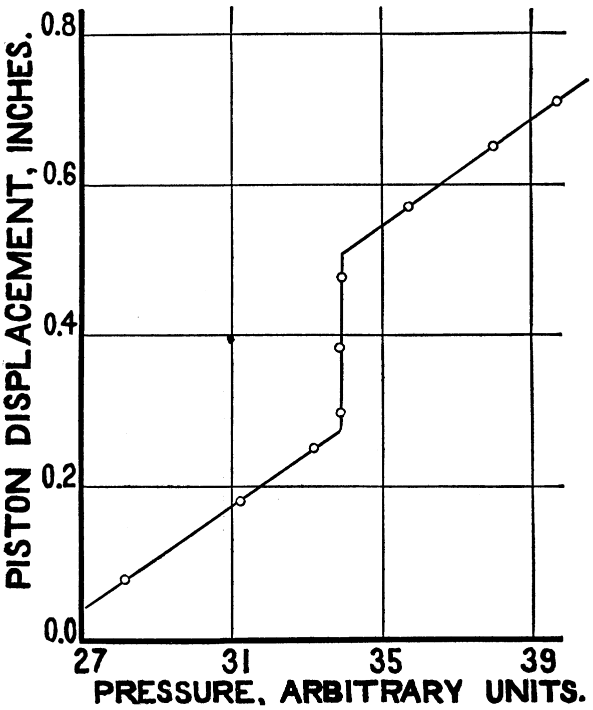

FIGURE 19. Shows the discontinuity in the piston displacement during freezing. (One division on the pressure axis corresponds to 900 kgm.)

closer to the upper corner of the curve, as will be shown in the magnified diagram later, but the lower corner cannot be approached very much more closely, because of the subcooling of the liquid mercury.

The data are collected in Table X. and shown in Figure 20. These data can be subjected to a calculation exactly like that used for the equilibrium points found by the change of resistance method. A straight line was passed through the midst of the points, the deviations from this line plotted on a large scale, and the best smooth curve drawn through the deviations. The calculated values were obtained from this smooth deviation curve and the original straight line. The points are not so regular here as for the determination by the change of resistance method, and the best smooth curve is open to greater question. The deviations from linearity are nearly twice that found by the resistance method, namely 140 against 60 kgm. at 12,000. This has

TABLE X.

Freezing Pressure of Mercury at Different Temperatures by the Method of Change of Volume.

Temp. °C.	Pressure, kgm./cm.^{2}.			
	Observed during Increase.	Observed during Decrease.	Observed Average.	Calculated [Linear Relation + Deviation Curve].
0.00	7570	7550	7560	7620
6.37	8905	8895	8900	8890
12.87	10230	10210	10220	10180
18.45	11360	11340	11350	11340
12.88	10130	10150	10140	10180
−19.9	3660	3660	3660	3700
− 9.8	5610	5570	5590	5680
0.00	7590	7590	7590	7620
9.16	9455	9445	9450	9440
16.4	10910	10910	10910	10900
5.23	8650	8670	8660	8680

as a result that the tangent at the origin as determined here gives a rise of pressure of 195.5 kgm./cm.^{2} per degree, against 196.5 found before, a difference of 1/2 per cent. The two series are not really so much different as this would indicate, because the smaller initial slope of this present series is unduly influenced by the very evident greater irregularity of the low-temperature points, and is compensated for by the greater departure from linearity. If we are willing to admit that the departure from linearity of the resistance measurements is probably more nearly correct, and apply this departure to the seven determinations by the present method above zero, we shall find as the average slope 196.3 kgm./cm.^{2} at the origin, agreeing within 1/10 per cent of the former value. In the rest of the work of this paper the best value for the slope at the origin will be taken as 196.4 kgm./cm.^{2} per degree, and the departure from linearity given by the resistance measurements will be taken as most probably correct.

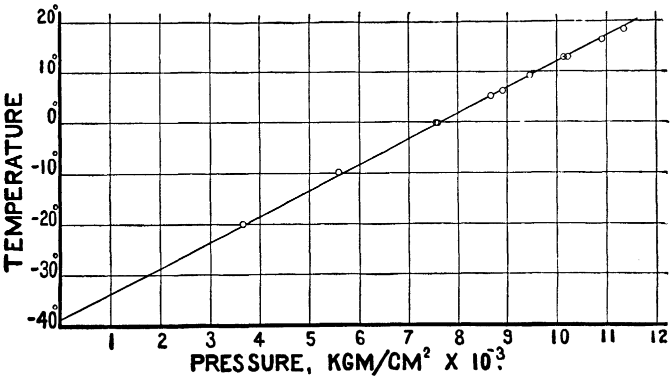

FIGURE 20. The equilibrium curve of liquid and solid mercury obtained by the change of volume method.

The changes of volume corresponding to these equilibrium pressures were all determined with the same set up of apparatus as already explained. These results are given in Table XI., and plotted against temperature on an enlarged scale in Figure 21. The observed values were obtained graphically from figures like Figure 19, drawn on a very much enlarged scale. For this purpose, it was not necessary to plot the actual pressures, but the position of the slider on the bridge wire on which the resistance measurements were made was used instead. This enables smaller changes of pressure to be measured with accuracy than could be done in the other way. The absolute gauge against which the calibration of the resistance was made has a limit of sensitiveness of about 8 kgm./cm.^{2}, while the resistance measurements are sensitive to about 2 kgm. The scale of the graphical construction was so enlarged that 1 cm. on the bridge wire goes into 5 cm. on the diagram, and 0.01 inch piston displacement into 1 cm. on the diagram.

TABLE XI.

Change of Volume of Mercury on Freezing as a Function of the Freezing Temperature.

Temp. °C.	Δv, cm.^{3} per gm.		
	Observed.	Corrected (1).	Corrected (2) final.
−19.9	0.002533	0.002503	0.002515
− 9.8	2498	2487	2492
0.0	2448	2458	2454
5.23	2410	2426	2426
9.16	2376	2399	2399
16.40	2315	2348	2348

Ordinarily four points were found on the curve both above and below the transition point, covering a range of from 500 to 700 kgm. in both directions. Over this range, and within the errors of reading, the curve connecting piston displacement with the position of the slider on the bridge wire was almost without exception linear, and was drawn in with a ruler. There was no tendency whatever for either corner of the melting curve to be rounded off, indicating that the change of state takes place at a single definite temperature and pressure, and affording the best possible evidence of the sufficient purity of the mercury. To this fact of absolutely sharp freezing is to be attributed the self-consistency of the results. With water, where there is some slight rounding off of the corners, the results are not so self-consistent, although the total change of volume is larger.

The process of correction applied to the observed values is shown in the table in two steps so as to give an idea of the magnitude of the corrections. In column (1) the corrections for the thermal dilatation of the kerosene on passing from the lower to the upper cylinder and the correction for the elastic deformation of the upper cylinder are both applied. In the second and finally corrected column, the additional correction for the variation of room temperature is applied. The sign of this correction changes with the direction of variation. As appears from the figure, these points are self-consistent, lying on a smooth curve to at least the order of accuracy given above, 1 part in 2500, except the point at 9° which is only 1/10 per cent out. The total displacement of the piston during freezing was about 0.2 inch, the quantity of mercury used being in the neighborhood of 350 gm. To obtain the above accuracy, therefore, it was necessary to take advantage of the utmost capacity of the micrometer, making all the readings to 0.0001 inch. That the single measurements do enjoy this degree of accuracy is made evident by a later very much enlarged figure drawn for the purpose of showing the impossibility of subcooling.

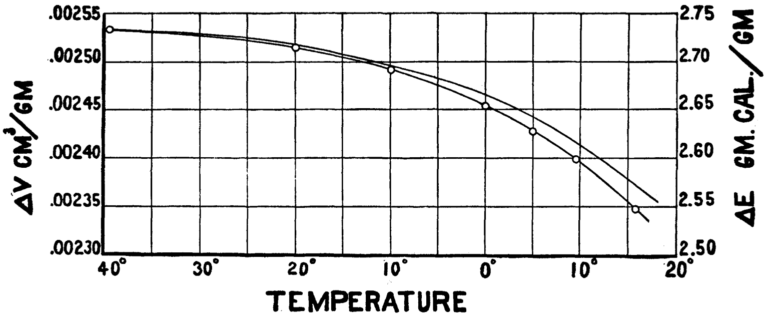

FIGURE 21. Shows the change of volume and of internal energy on passing from the liquid to the solid. The change of volume curve was directly observed, and the experimental points are indicated. The change of energy curve was calculated from the other data.

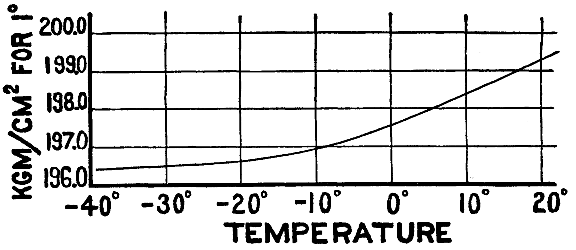

FIGURE 22. Shows the slope of the freezing curve as a function of the equilibrium temperature.

It is not claimed, however, that the absolute values at the high pressures have quite so much accuracy as this self-consistency would indicate, since probably the correction for the distortion of the upper cylinder leaves room for greater uncertainty than this.

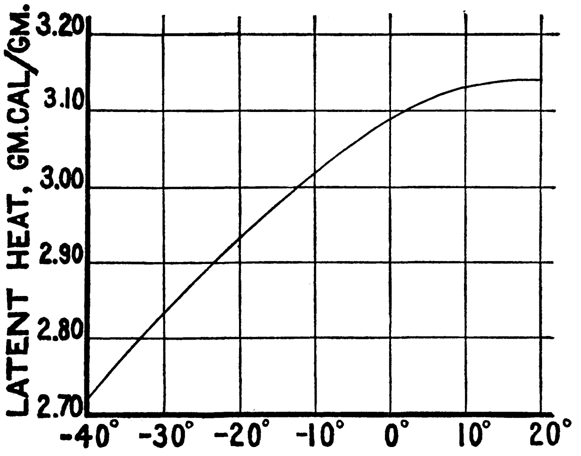

FIGURE 23. The latent heat of solid mercury as a function of the equilibrium temperature.

It is gratifying to notice that the point determined at atmospheric pressure by an entirely different method agrees perfectly with the points found above, making the accuracy of both determinations very probable.

From these data the latent heat of transformation may be found at every point of the melting curve by Clapeyron's equation,

$$\Delta H = \tau \Delta v \frac{dp}{d\tau}.$$

ΔH was calculated from this equation at intervals of 10° from $-40°$ to $+20°$. $\frac{dp}{d\tau}$ was found by adding to the constant value 196.4 kgm. per degree the correction found from the graphically constructed slope of the curve showing the departure of the curve from linearity. The results of this graphical construction are shown in Figure 22. The absolute zero in the calculation was taken as $-273°.1$ C. The results in mean gm. cal. per gm. of mercury are shown in Figure 23 and Table XII.

The rise of ΔH to a probable maximum is the most interesting feature. The course of this curve is to be explained by the increasingly rapid drop of ΔV at high pressures, this drop finally becoming more rapid than the increase in $\frac{dp}{d\tau}$ and in the absolute temperature.

TABLE XII.

Change of Latent Heat on the Freezing Curve of Hg.

Temperature.		Δv cm.^{3} per gm.	$\frac{dp}{dt}$ gm./cm.^{2}.	Latent Heat mean gm. cal. per gm.
°C.	Abs.			
−40	233.1	0.002535	196400	2.720
−30	243.1	2526	196500	2.828
−20	253.1	2515	196600	2.939
−10	263.1	2492	196900	3.025
0	273.1	2454	197600	3.103
+10	283.1	2393	198350	3.149
+20	293.1	2311	199300	3.163

It will be noticed here, as for the change of volume, that the curve does not give the usually quoted value for the heat of transformation at $-38°.85$, but here also it seems that there is considerable chance for error in the previous value. The value always given is 2.82, which was obtained by Person[43] in 1847. As far as can be discovered, this is the only determination of this quantity which has ever been published. Person's method consisted essentially in dropping the frozen mercury at a temperature of about $-42°$ into the water or turpentine of a calorimeter, and noting the fall of temperature. The usual corrections for radiation and the heat capacity of the vessel were applied. The actual heat given to the calorimeter was the sum of the heat given out by the solid in cooling to the transformation point, the heat of transformation, and the heat of the liquid in warming to the temperature of the calorimeter. The value $C_p = 0.0333$ was assumed to hold for the liquid over the temperature range. This is probably nearly correct, but the assumption that C_p for the solid is the same as for the liquid is probably open to greater question. The error introduced by this cannot be very large, however, because of the small temperature range over which the solid cooled. By far the greatest possibility of error seems to be in the simple measurement of temperature. The thermometry of low temperatures must have been in a chaotic state at the time, judging by the values given by Person for known fixed temperatures. He gives the value on the air thermometer of the melting point of mercury as —41°. This point is now known to be — 38°.85. He furthermore states that his alcohol thermometer read higher than a mercury thermometer at — 20°. No statement whatever is made as to the corrections applied to the readings of this alcohol thermometer. If, however, he did apply the correction of the mercury thermometer to the alcohol thermometer, then there is still the possibility of great variation between — 20° and — 40°. The consistent behavior of three calibrated alcohol thermometers which have been used in this present work indicates a possibility of error of as much as 3 per cent between — 20° and — 40°.

---

[43] Person, Ann. de Chim. et Phys., **24**, 257–264 (1848).

Person made three determinations of the latent heat, giving 2.77, 2.86, and 2.83, mean 2.82, as against 2.735 found above. The use of this latter value seems to be justified, therefore, in preference to that of Person.

Person's value for the latent heat has entered directly into the determination by Regnault[44] in 1849 of the specific heat of solid mercury. Again the value of Regnault is apparently the only value which we have of this quantity. The method of Regnault was exactly the same as that of Person, except that the mercury was initially at — 77°.7, so that the heat given out by the solid in cooling to the melting point was a very appreciable part of the total heat given out. Incidentally Regnault's temperature measurement was very probably at fault as well as Person's, for he gives — 40° as the melting point of mercury. Regnault made two determinations of the mean specific heat from — 77°.7 to the melting point, giving 0.0314 and 0.325. Evidently the effect of a smaller latent heat of melting would be to give a larger specific heat to the solid. Substituting the value found above produces a change of 6.5 per cent in the values given by Regnault, giving 0.0334 and 0.0346 respectively, mean 0.0340.

The data used in determining the change of volume may also be used to give evidence on one point for which they were not intended. The slope of the curve plotting piston displacement against pressure is evidently going to be different above and below the melting point because of the difference in compressibility between the solid and the liquid mercury. The compressibility of mercury is small in any event, and here the greater part of the piston displacement is used in compressing the kerosene, so that only rough values can be expected from the small difference. There is the further complication of the drift in the temperature of the room. The slope does show a distinct tendency to be less when the solid state is present, but the change is irregular. It can be said, however, that the compressibility of the solid at the freezing point is less than that of the liquid, the difference being in the neighborhood of 10 per cent.

---

[44] Regnault, Ann. de Chim. et Phys., **26**, 268–278 (1849).

THE CHANGE OF VOLUME OF MERCURY ON FREEZING AT ATMOSPHERIC PRESSURE.

It has already been stated that the necessity for redetermining the change of volume at atmospheric pressure arose from the probable inaccuracy of the previously accepted value (0.00260 cm.^{3} per gm.). The inaccuracy of this number was first suspected when a set of values found for Δv at different pressures, consistent among themselves to 1/25 per cent, did not extrapolate to within 2 per cent of 0.00260. Investigation showed that the value 0.00260 is not a direct experimental determination, but is obtained from the difference between the density of the solid, as found by one observer, and the density of the liquid as given by another. Since the change of volume is only about 3 per cent of the total volume, the density of both solid and liquid must be known with an accuracy of sixty times the accuracy desired in the change of volume. The following short discussion of these previous experimental determinations will make clear that there are here possibilities of error of fully the indicated magnitude.

The value of the density of the solid seems to be open to by far the most serious question. The commonly accepted value, in fact the only value with any claim to accuracy at all, was given by Professor Mallet[45] of the University of Virginia. The method consisted in freezing a weighed quantity of mercury in a glass bulb, and then determining the quantity of alcohol necessary to fill the bulb to a fixed mark. The largest possibility of error seems to be in determining the volume of the bulb at the freezing temperature of mercury. This was found from the quantity of mercury filling it at 0° and 100°, using Regnault's value for the dilatation of mercury, and extrapolating back to the freezing point. No account at all was taken of the possibility of permanent changes of volume of the glass bulb after subjecting to 100°. That there is such an effect, very noticeable, is shown by the change of zero of glass thermometers after subjecting to a high temperature. No mention is made of the kind of glass; if it were an American lead glass, the effect would be comparatively large. The final value for the density of the solid as given by Mallet was 14.1932. This is the mean of three values, 14.1948, 14.1920, and 14.1929.

---

[45] Mallet, Proc. Roy. Soc. Lon., **26**, 71 (1877).

The density of liquid mercury at the freezing temperature is given in Landolt and Börnstein's tables as coming from Vicentini and Omodei,[46] but the value given by them is as a matter of fact quoted from a paper of Ayrton and Perry.[47] Their method consisted in reading simultaneously the same temperatures between 0° and —38°.85 with a mercury in glass thermometer and an air thermometer. The readings of one plotted against the other are stated to be "very nearly linear," from which the conclusion is drawn that the dilatation of mercury between 0° and —38°.85 has the same constant value as that found by Regnault to hold between 0° and +100°. The density at —38°.85 is then calculated from the known density at 0°. No statement whatever is made as to the degree of accuracy attained, or even as to the direction in which the plot of the air against the mercury thermometer departs from linearity. However, the fact that one of the conclusions drawn from the results is that mercury shows no maximum of density in the neighborhood of the freezing point analogous to water, suggests that the previous knowledge of this quantity was very imperfect indeed, and that the results of Ayrton and Perry themselves are not so accurate as necessary for the present purpose.

A direct determination of this change of volume with the same apparatus as was used at higher pressures and temperatures would have been possible, but inconvenient for several reasons. Chief of these was the difficulty of running a thermostat of the requisite size with sufficient constancy at this low temperature. Furthermore, if a result concordant with the others could be found by an entirely different method, the results by the two methods would mutually support each other, making any consistent error in either improbable.

The method used consisted in weighing a known quantity of mercury under CS_2 at different temperatures in the neighborhood of the melting point. The weight varies with the temperature. When the temperature passes through the melting temperature, the mercury melts with increase of volume, and the increased displacement causes a sudden change in the weight equal in amount to the weight of the displaced CS_2, that is, equal to the weight of CS_2 of volume equal to the change of volume of the mercury. The only quantities directly concerned are the discontinuity of the weights and the density of the CS_2 at the point of discontinuity. It is not necessary to know even the temperature accurately. Any consistent device for indicating changes of temperature, so that the weight may be plotted as some continuous function of the temperature on either side of the melting point, is all that is required.

---

[46] Vicentini and Omodei, Atti di Torino, **23**, 38–43 (1887–1888); and **22**, 28–47, 712–726.

[47] Ayrton and Perry, Phil. Mag., **22**, 325–327 (1886).

The temperature was indicated by the resistance of a coil of fine double silk covered iron wire, wound on a glass core 4 inches long and placed in kerosene inside a thin-walled brass tube, which was immersed directly in the CS_2 in which the weighings were made. The coil was not calibrated for absolute temperature, but the resistance could be measured with an accuracy corresponding to changes of temperature of 0°.002. In addition, the temperature was read on a toluol thermometer, graduated to 0°.1, which was also immersed in the bath. The readings of the thermometer were taken only to give a check on the readings of the resistance thermometer, since the thermometer readings were inaccurate because of varying parallax and the necessity of removing the thermometer partly from the bath in making the readings.

The cold CS_2 in which the mercury was weighed was contained in a cylindrical Dewar flask, 2 inches in diameter and 12 inches long. The inside of this was lined with a sheet of celluloid to protect the glass from being scratched, and inside this a tube of heavy copper tubing, 5/32 inch thick, to promote rapid equalization of the temperature. The most effective equalization of temperature, however, was provided by a small turbine stirrer, reaching the entire length of the flask. This was run constantly between readings, but was naturally stopped while a weighing was being made. The mercury was contained in a thin steel shell, 9/16 inch diameter, and 4 inches long, suspended by a fine iron wire (0.007 inch diameter), from the beam of a sensitive balance above. The quantity of mercury used was about 140 gm. It was possible to weigh this to 1/4 milligram, giving an accuracy on the discontinuity of weight on freezing, which was about 0.6 gm., of one part in 2000. In the respect of sensitiveness, the CS_2 is probably as convenient a liquid as could be found, because of the high density and very low viscosity and surface tension. Provision was made for warming the bath after each weighing by passing a current through a small heating coil immersed in the bath.

The experimental procedure was the natural one. The Dewar flask was first filled with CS_2 which had been cooled in another dish with

CO_2 snow and ether. In this was suspended the steel shell with the mercury, which had been previously frozen. The temperature was then raised to about —42°, and readings made at intervals of 0°.5. The spontaneous rise of temperature of the bath during a weighing was so small as to introduce no error. During warming, the weight increases linearly, due to the larger thermal expansion of the CS_2 than the mercury. Melting is indicated by a rapid drop in the weight of about 0.6 gm. This drop is not instantaneous, but may extend over 1°.5, showing temperature lag between the mercury and the bath while the heat of transformation is being absorbed. Completion of melting is indicated by resumption of the linear relation between weight and temperature. To find the discontinuity in the weight, it is merely necessary to extrapolate this straight line back to the point at which melting began.

There are only a few special precautions to observe. The most likely source of error is the formation of minute cracks in the mercury when freezing. To obviate this, the mercury was poured into the steel shell already filled with CS_2, so as to ensure filling of all the corners, and then frozen by placing merely the very bottom of the shell in the freezing mixture. Freezing took place very slowly and uniformly from the bottom, the surface of the finally frozen mercury being as perfectly convex as that of the liquid. Pains had to be taken to scrape away from time to time the minute quantities of ice condensing on the suspending wire. This wire was so fine that no correction whatever had to be applied for the slightly varying depths of immersion during the course of an experiment. Finally, it was necessary to determine the density of the CS_2 at the freezing temperature separately for each experiment. This arose from the fact that during the preliminary work a slight quantity of ether had been accidentally spilled into the CS_2, enough to decrease the density by 1 per cent. This gradually evaporated, producing a slow rise in the density of the CS_2 to a final steady value. The density was given directly by the loss of weight of the mercury and steel in the CS_2 at the freezing temperature. There seems no question whatever but that the density of the liquid mercury at the freezing point is known with the accuracy demanded here, 1 part in 2000, although there may be reasonable question as to whether its accuracy is 60 times greater, as it must be when used to give the change of volume by a subtraction. The steel shell was only a small part of the total weight, and its thermal dilatation is so well known and so small that there is no danger at all in calculating the density of the steel at −38°.85 from the experimentally measured density at room temperature. The accuracy of this procedure is vouched for by the fact that the density of the CS_2 when determined by weighing in it a solid steel cylinder agreed within 1 part in 13,000 with the value found by weighing in it the steel shell with the mercury.

Five preliminary determinations of the change of volume were made giving results varying from 0.00253 to 0.00257. The chief cause of inaccuracy in these preliminary results was the irregular behavoir of the resistance thermometer. This was due to the defective insulation of the enamelled wire used in these first experiments. Replacing the enamelled wire by silk-covered wire gave perfectly satisfactory results. Advantage was also taken of this preliminary work to modify slightly various details of apparatus and procedure.

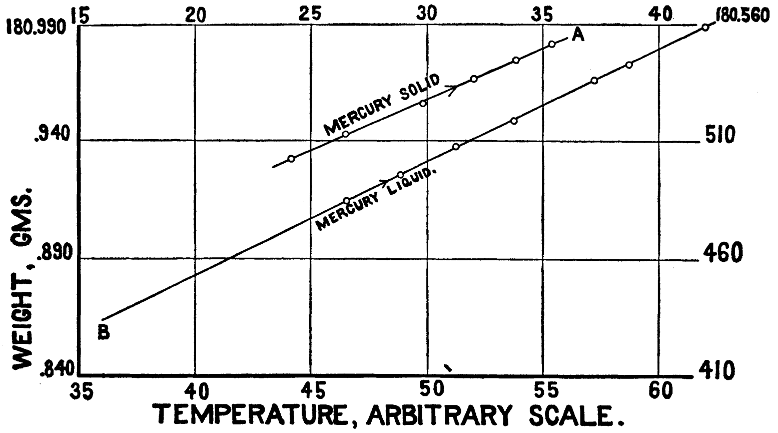

Figure 24. Shows the readings from which was found the change of volume when mercury melts at atmospheric pressure. The scale above and to the left refers to the solid mercury, and that below and to the right to the liquid. The point A indicates the beginning of melting, and the point B shows the completion of melting.

Three independent determinations of the change of volume were made with the final form of apparatus. The experimental points of one of these determinations are shown in Figure 24. The mercury was changed for each of these determinations, the total quantity being varied by 10 per cent. The three values found, using the iron resistance as the temperature indicator, were 0.002533, 0.002536, and 0.002532 $cm.^3$ per gm. The same weighings plotted against the thermometer readings (it is to be remembered that this was done merely as a check) gave 0.002533, 0.002537, and 0.00252 respectively. The thermometer points of the last determination were very irregular.

The resistance points are to be taken as the correct ones, and the mean of the three determinations, 0.002534, is accepted as the best value. The departure from the previous value, 0.00260, is thus nearly 3 per cent.

This result may be used to give a more accurate value than that of Mallet for the density of the solid mercury at the freezing point. Assuming for the density of the liquid at the freezing point the value of Ayrton and Perry, 13.690, the density of the solid is found to be 14.182 as against 14.193 of Mallet.

This also enables a correction to be applied to the value of the coefficient of dilatation of solid mercury as found by Dewar.[48] He determined the density at —188°.7 (in liquid air) and from Mallet's value for the density at the freezing point calculated the coefficient of thermal dilatation to be 0.0000887 over the range from —38°.8 to —188°.7. Substituting the above value for that of Mallet gives 0.0000907. Dewar's value for the density of mercury at the temperature of liquid air seems open to question, however. All of Dewar's measurements of density at low temperatures depend on his value for the density of liquid oxygen, which he gives as 1.137. The measurements which he made on ice would seem to show a probable error here. The value for the thermal dilatation of ice over the range 0° to − 190° was found to be only half the known value from 0° to — 20°. So large a decrease seems hardly probable. A change in the fundamental constant so as to give a higher value to this dilatation would also give a higher value to the thermal dilatation of mercury. Furthermore, a change in this direction would bring Dewar's value for the dilatation of mercury into agreement with that of Grunmach,[49] namely, 0.000123 from — 38° to — 80°. This is apparently the only other value we have. But Grunmach used a dilatometer method in which he made no correction whatever for the effect of the glass envelope. The value obtained by him for the change of volume on freezing with the same apparatus is certainly wrong, namely, 5 per cent as against 3 per cent found above, and this one fact is enough to cast discredit on the rest of the work. There seems to be no value, therefore, which can be accepted at present with confidence for the thermal dilatation of the solid.

In view of the apparent uncertainty as to the value of the thermal dilatation of the solid, it may perhaps be allowed to force the above weighings to give what information they can on this point. It is not expected that the value so obtained can do more than roughly indicate the probable value, since this use of the data was not contemplated in the original experiment. The information comes by observing at the melting point the change in the slope of the curve plotting weights against temperature. The slope is evidently connected with the various thermal dilatations.

---

[48] Dewar, Proc. Roy. Soc. Lon., **70**, 237–246 (1902).

[49] Grunmach, Phys. ZS., **3**, 133–136 (1902).

The exact expression is found to be

$$\left(\frac{d\bar{W}}{dt}\right)_1 - \left(\frac{d\bar{W}}{dt}\right)_2 = \frac{dD_{CS_2}}{dt}\left[V_{Hg,2} - V_{Hg,1}\right] - D_{CS_2}\left[\left(\frac{dV_{Hg}}{dt}\right)_1 - \left(\frac{dV_{Hg}}{dt}\right)_2\right].$$

The subscript 1 refers to the liquid and 2 to the solid. D_{CS_2} is the density of the CS_2. The value $\frac{D_{CS_2}}{dt}$ was taken to be 0.0014. This amounts to assuming the value of the dilatation of CS_2 to be 0.001, which is the value given at 0° by Pierre's formula. There is room for considerable question here, but the term into which $\frac{D_{CS_2}}{dt}$ enters is only 10 per cent of the other term involving the dilatation of the liquid mercury.

Only the last two of the sets of weighings are available for this calculation, the CS_2 having then assumed an unvarying value for the density. The dilatation of the solid calculated from these two sets was 0.000165 and 0.000125, mean 0.00014. The value is extremely rough, but probably as good as either the value of Dewar or Grunmach.

These data also give a rough incidental determination of the density of CS_2 at $-38°.85$. This was found to be 1.3460. It has been already mentioned that this is probably slightly in error due to the presence of a slight impurity of ether, but the above value was the final value, and remained constant over two days, showing that what little ether there was had nearly all evaporated. The density as calculated by the third degree formula of Isid. Pierre is 1.3647.[50] The formula of Pierre is intended to hold only for the range 0° to 100°. The discrepancy suggests at any rate the danger of using the formula by extrapolation to considerable negative temperatures.

SUBCOOLING AND SUPERHEATING.

All these observations on the freezing and melting of mercury under pressure also show that one property which apparently holds without exception at atmospheric pressure also holds under high pressure. This is the fact that it is impossible to superheat a crystalline phase with respect to the liquid phase, although the liquid may be subcooled, sometimes very considerably, with respect to the solid. Figure 25, drawn on a very large scale, shows this fact. At the lower corner the subcooling of the liquid with respect to the solid is shown, while at the upper corner, where the pressure is decreased on the solid phase, is shown the sharp change of state when the equilibrium pressure is overstepped. The slight irregularities in the points are due to errors of

---

[50] Pierre, Ann. de Chim. et Phys. (3), **15**, 325 (1845).

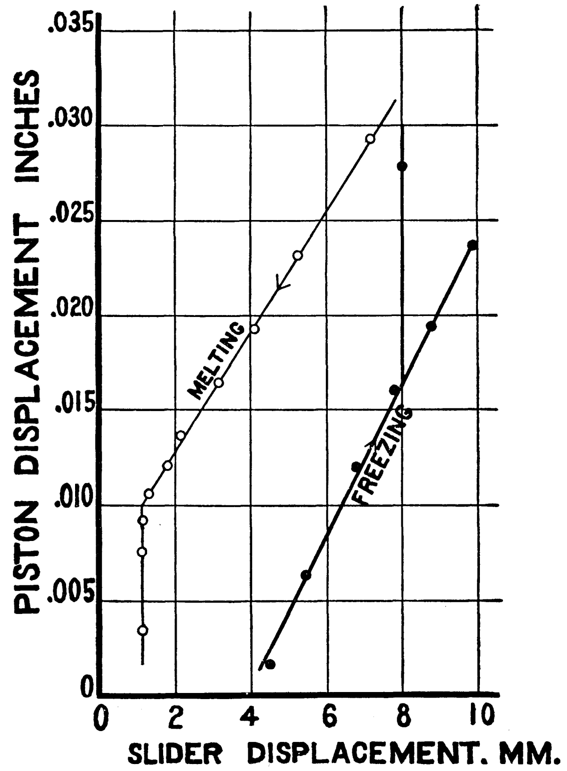

FIGURE 25. Shows on an enlarged scale the possibility of subcooling the liquid but the impossibility of superheating the solid. The two curves have been displaced, the one with respect to the other; the melting and freezing actually takes place at the same pressure. One division on the pressure axis corresponds to 40 kgm.

reading, the several points on the vertical part of the curve at decreasing pressure differing among themselves by only 0.05 mm. of bridge wire, better than the limit of reading, corresponding to pressure differences of 1 kgm./cm.^{2}. The points plotted are the mean of two readings, each to 0.1 mm. The same possibility of subcooling was found during measurements by the change of resistance method.

Attempts to measure the amount of subcooling would have had no absolute value, for its amount depends on many extraneous factors, such as the size and shape of the glass capillary, the presence of small particles of grit in the fluid transmitting pressure, and most important of all, the element of time. The greatest amount of subcooling found from the resistance measurements was 230 kgm. at 10°.2, equivalent to about 1°.1. The mercury remained liquid under these conditions for about 30 minutes, and did not freeze until the pressure was still further increased.

This impossibility of superheating a crystal has been shown to be so universally true that it is coming to be regarded in the light of a natural law. It holds whether the liquid melts with increase or decrease of volume. No satisfactory explanation has yet been given of the fact, however. Nearly all the explanations suggested, applicable at atmospheric pressure, have attempted to make it in some way a surface phenomenon, the melting beginning at the free surface and running in toward the interior. In view of the fact shown above that superheating is also impossible under very high pressures, it would seem somewhat doubtful whether this is the correct method of attack on the problem. Under high pressures the surface of separation between the solid and the surrounding liquid (mercury and kerosene, for example) cannot be thought of properly as a free surface. The molecules of mercury would seem no more free to assume their natural positions at this surface than they would in the interior of the mercury itself. This is particularly probable when it is remembered that the mercury melts with increase of volume.

Conclusion.

In this conclusion an attempt will be made to show what bearing the data may have on the theories of the liquid state and on our knowledge of the change of state liquid-solid. As giving the best general survey of all the data, a diagram is presented showing the isothermal lines for the liquid and the sudden change on passing to the solid state. (Plate.) The data from which this figure was constructed are shown in Table XIII. Within the accuracy of this work the isothermals may be taken as equi-spaced, as already explained. The first thing to strike one on looking at the diagram is that the effects are nearly constant over the entire range; the compressibility does not change markedly, nor does the dilatation, and the lines bounding the domain liquid-solid are nearly parallel. It is evident, therefore, that any reversal of the ordinary effects or the appearance of critical points must be far beyond the reach of the diagram. The diagram is competent to show only the initial trend of the various effects.

TABLE XIII.

Points on the Isothermals of Liquid Hg.
(Computed from Experimental Curves at 0° and 22°.)

Pressure, kgm./cm.^{2}.	Volume, cm.^{3}.					
	—30°.	—20°.	—10°.	0°.	+10°.	+20°.
0	0.99457	0.99638	0.99819	1.00000	1.00181	1.00362
1000	99207	99280	99553	0.99626	0.99799	0.99972
2000	98760	98927	99094	99261	99428	0.99593
3000	...	98581	98743	98905	99067	99232
4000	...	98245	98403	98561	98719	98877
5000	...	...	98077	98231	98385	98540
6000	...	...	97763	97914	98065	98216
7000	...	...	...	97607	97756	97904
8000	...	...	...	...	97461	97608
9000	...	...	...	...	97182	97327
10000	...	...	...	...	96915	97059
11000	...	...	...	...	...	96806
12000	...	...	...	...	...	96567
Change of vol. on freezing	0.03435	0.03418	0.03388	0.03337	0.03243	0.03142
Freezing pressure	1740	3710	5670	7640	9620	11600

For the liquid state the results are the same in general as those with which we are familiar for the more compressible liquids under lower pressures. The compressibility and the dilatation both decrease with rising pressure. This has as a consequence that the effect of rising temperature is as usual to increase the compressibility. The behavior of the specific heats is rather unusual, approximate constancy for C_p and increase of C_v with pressure. For water, $C_p - C_v$ increases instead of decreasing. As a little surprising, but not unusual, it may be mentioned that the internal energy decreases along an isothermal with increasing pressure, but increases, as is normal, along an adiabatic. This means that along an isothermal the attractive force between the molecules is still the dominant factor in the situation, even up to 12,000 kgm. At higher pressures a reversal of the effect is indicated, where the repulsion between the molecules would become the important part.

The data are more suggestive in the light they throw on the change from the liquid to the solid state. In this connection it may be useful to outline briefly the present state of the theory, and the points at issue.

For the change of state liquid-vapor, the physical facts have been worked out pretty fully until we now have a fairly definite understanding of the nature of the process. This increase of knowledge has come about almost entirely from the experimental side, the one thermodynamic relation not being of much assistance. In particular, the existence of the critical phenomena, and the possibility of the continuous passage from the liquid to the vapor were facts which were unexpected before the actual experimental proof. There is no thermodynamics which would predict the existence of such a point. Our present knowledge of the nature of the equilibrium between liquid and solid is in much the same state as the knowledge of the transformation liquid-vapor before the discovery of the critical point. The fundamental question as to whether a critical point exists or not is therefore of greatest immediate interest.

At present, both the most important theory of the equilibrium between solid and liquid and the most far reaching experimental work are due to Tammann.[51] The essential part of his theory, as opposed to Ostwald,[52] Poynting,[53] and others, is that for the transition solid-liquid there is no critical point like that for the transition liquid-vapor. The reason for this fundamental distinction is to be found in the essential similarity between a liquid and a vapor on the one hand, and the essential dissimilarity between a liquid and a crystal on the other hand. The molecules in both the liquid and the vapor are thought of as arranged at random, "molekular-ungeordnet," the only difference between liquid and vapor lying in the average distance apart of the molecules. Once let the average distance apart of the molecules appropriate to the vapor and liquid become equal, as they do at the critical point, and all further distinction between the two phases vanishes. In particular, the heat of transformation vanishes as a consequence of the equality of the volumes. But for the two phases liquid-crystal, there is besides the distinction of density the further distinction that in the crystal the molecules are arranged in some sort of a framework in space. Equality of density of the two phases liquid and solid does not mean identity, because the crystal still preserves the regular arrangement of the molecules which cannot hold in the liquid. In consequence, the energy difference between the two phases need not become zero when the volume difference vanishes; that is, the heat of transformation does not vanish at the same time with the change of volume, and we do not have a critical point. Tammann goes further than simply to deny the existence of a critical point. He concludes from an examination of all the known data, chiefly his own experiments, that for substances of the ordinary type of freezing with decrease of volume, not only do the change of latent heat and the change of volume fail to pass through the value zero at the same time, but that the change of volume always becomes zero before the heat of transformation. It is then an immediate deduction from Clapeyron's equation that the melting curve has a maximum. That is, there exists for every substance a temperature so high that no pressure, however intense, will bring the point of transition as high as this temperature. Above this temperature the substance is always liquid. This is really the essential part of Tammann's theory of the shape of the equilibrium curve. It has been immediately seized upon by geologists, and made the basis of many speculations as to the state of the interior of the earth, the matter there being supposed fluid because the temperature is higher than the maximum.

---

[51] Tammann, loc. cit.

[52] Ostwald, Lehrbuch der Allgemeinen Chemie, II^{II}, Verwandtschaftslehre, p. 389 (Engelmann, Leipzig, 1902).

[53] Poynting, Phil. Mag. (5), **12**, 32 (1881).

The experimental evidence in support of this theory is meagre, the pressure reached by Tammann being sufficient only to show a curvature in the direction demanded by the presence of a maximum, and an initial decrease toward zero of the change of volume more rapid than the decrease of the latent heat. The only case in which Tammann claims to have found a maximum, for $Na_2SO_4 10H_2O$, must be ruled out because of the complication introduced in the equilibrium conditions by the water of crystallization.

The evidence of the present data of significance for this question as to the existence of either a critical point or a maximum are the slope of the freezing curve, the variation of volume, and the variation of the latent heat.

The freezing curve is concave toward the pressure axis, which is curvature in the direction demanded by the presence of a maximum. This direction of curvature is the same as that shown by all the melting curves of Tammann, who uses it as an argument tending to show the existence of a maximum. But the curves liquid-vapor also invariably show the same curvature, and here there is a critical point. It is also easy for a curve to run to infinite temperature and pressure, still being concave toward the pressure axis. The direction of curvature would seem to give absolutely no presumptive evidence, therefore, one way or the other.

The change of volume and the latent heat together may be considered. The change of volume alone invariably decreases with rising temperature. This merely means that the phase with the smaller volume is less compressible. Tammann's argument consists in showing that the change of volume decreases along the equilibrium curve, while the latent heat usually increases, or if it shows a decrease, the decrease is slight in comparison with the decrease in the change of volume. The change of volume becomes zero first, therefore, and we have a maximum freezing temperature.

The curves for ΔV and the latent heat of this present work on mercury have been already shown. ΔV decreases with rising temperature, as it does universally. The latent heat curve is the significant curve, because it increases apparently to a maximum and seems about to descend. Tammann's argument would be perfectly valid for the first 6000 or 7000 kgm., but at higher pressures this reversal of the latent heat curve invalidates the whole thing. There is no reason to anticipate that the decrease in ΔH beyond 11,000 might not be rapid enough to make it vanish with ΔV.

It is interesting in this connection to plot the difference of internal energy between the solid and the liquid against temperature. The difference is given by

$$\Delta E = \Delta H - p\Delta v.$$

ΔE shows the part of the heat of transformation which has been made potential inside the mass. The rest of this heat goes into performing mechanical work. The results are shown, with the steps of the calculation in Table XIV. and in Figure 21, in direct comparison with the changes of volume. The energy decreases from the start along the equilibrium curve in such a way that its ratio to Δv is nearly constant. There seems no particular reason why this is not as significant a quantity on the melting curve as the latent heat. It is true that it does not enter the equations so simply, but the behavior at the points of special interest on the melting curve is just as simple as that of ΔH. At the critical point, for example, if there is one, where Δv becomes zero, but $\frac{d\tau}{dp}$ remains finite, it is known that $\Delta H = 0$. In this case $\Delta E = 0$ also. If the melting curve shows a maximum, which is characterized by $\Delta v = 0$, and $\frac{dp}{d\tau} = 0$, then ΔH remains finite, as does also ΔE, which in this case equals ΔH. The trend of ΔE on the melting curve would seem therefore to be just as valuable an indication as the trend of ΔH as to the possible existence of a critical point or a maximum.

TABLE XIV.

THE CHANGE OF INTERNAL ENERGY OF MERCURY ON PASSING FROM THE LIQUID TO THE SOLID AT DIFFERENT TEMPERATURES.

Temp. °C.	Pressure, kgm./cm.^{2}.	Δv cm.^{3} per gm.	Work $(=p\Delta v)$ gm. cal.	Latent Heat.	ΔE $(\Delta H - p\Delta v)$ gm. cal. per gm.
−28.66	2000	0.002525	0.118	2.848	2.732
−18.48	4002	2512	.235	2.951	2.717
− 8.31	6005	2486	.350	3.041	2.693
+ 1.87	8018	2443	.459	3.114	2.657
+12.06	10034	2377	.557	3.154	2.599
+22.24	12064	2296	.649	3.165	2.516

The present data offer no evidence, therefore, as to the existence of a critical point, except to show that if there is one it must be at pressures higher than can be reached directly. The positive result is obtained, however, that at high pressures there is a reversal in the behavior of the latent heat such as to invalidate Tammann's argument for a maximum.

As opposed to Tammann's argument for the impossibility of the existence of a critical point solid-liquid, it may be shown that it is possible to conceive of a molecular mechanism by which the continuous passage from the "molekular ungeordnet" assemblage of the liquid to the regular arrangement of the crystal on a space framework may be accomplished. We may think of the molecules as cubes, for example, with intense centers of force at the corners. As the molecules wander past each other in the liquid state, there will be a tendency for them to linger with the edges or the faces in contact. If the time during which they so linger in symmetrical positions with respect to each other becomes appreciable with respect to the total time, we will have some approach to the properties of a crystal, the approach becoming closer as the time of contact becomes relatively greater. And entirely aside from the question of molecular structure, there seems no difficulty in conceiving that if the temperature and pressure are varied properly on a cubical crystal, for example, that the three elastic constants might so change with respect to each other that two of them should eventually become equal, giving the two distinctive constants of an isotropic body, and so continuous passage from a crystalline to an amorphous body.

SUMMARY OF RESULTS.

Data have been collected in this paper sufficient to give the p-v-t surface of the liquid, and the location and magnitude of the discontinuity in this surface when the liquid freezes to the solid over a pressure range of 12,000 kgm./cm.^{2}, and a temperature range from $-38°.85$ to $+20°$. Tables of various quantities of thermodynamic interest are given for the liquid; such as the compressibility, the dilatation, the change in the specific heats, the adiabatic compressibility, the heat of compression, and the change in internal energy both along an isothermal and along an adiabatic. For the change liquid-solid the co-ordinates of the melting curve are given, the change of volume, and the latent heat. The results do not show any behavior in the liquid at high pressures opposite in character from that which would be predicted from their trend at lower pressures. But for the change solid-liquid, it seems that at high pressures there is a change in the trend of the latent heat which invalidates Tammann's argument for the existence of a maximum. If either a maximum or a critical point exist for the transition solid-liquid it is at pressures higher than are at present open to direct realization. Such a point could not well exist at less than 50,000 kgm./cm.^{2}.

Apart from the main work of the paper a number of other quantities relating to mercury have been determined, some of them very roughly, either by a direct calculation from the new data given here, or else by a recomputation from the data of others, using in this recomputation some of the improved values found here. These new quantities are: a more accurate value for the density of the solid at —38°.85, a rough value for the thermal dilatation and the compressibility of the solid, an improved value for the specific heat of the solid, the electrical resistance of the liquid up to the freezing pressure, and the resistance of the solid under pressure, including the pressure and the temperature coefficients.

Finally, the computations made necessary the determination of another quantity of interest in itself, namely, the compressibility of steel. This was determined up to 10,000 kgm. and at two temperatures, from which the temperature coefficient of compressibility is found.

Acknowledgement is here made of several liberal appropriations from the Rumford Fund of the American Academy of Arts and Sciences with which the expenses of this investigation were partially defrayed.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASS.
OCTOBER, 1911.

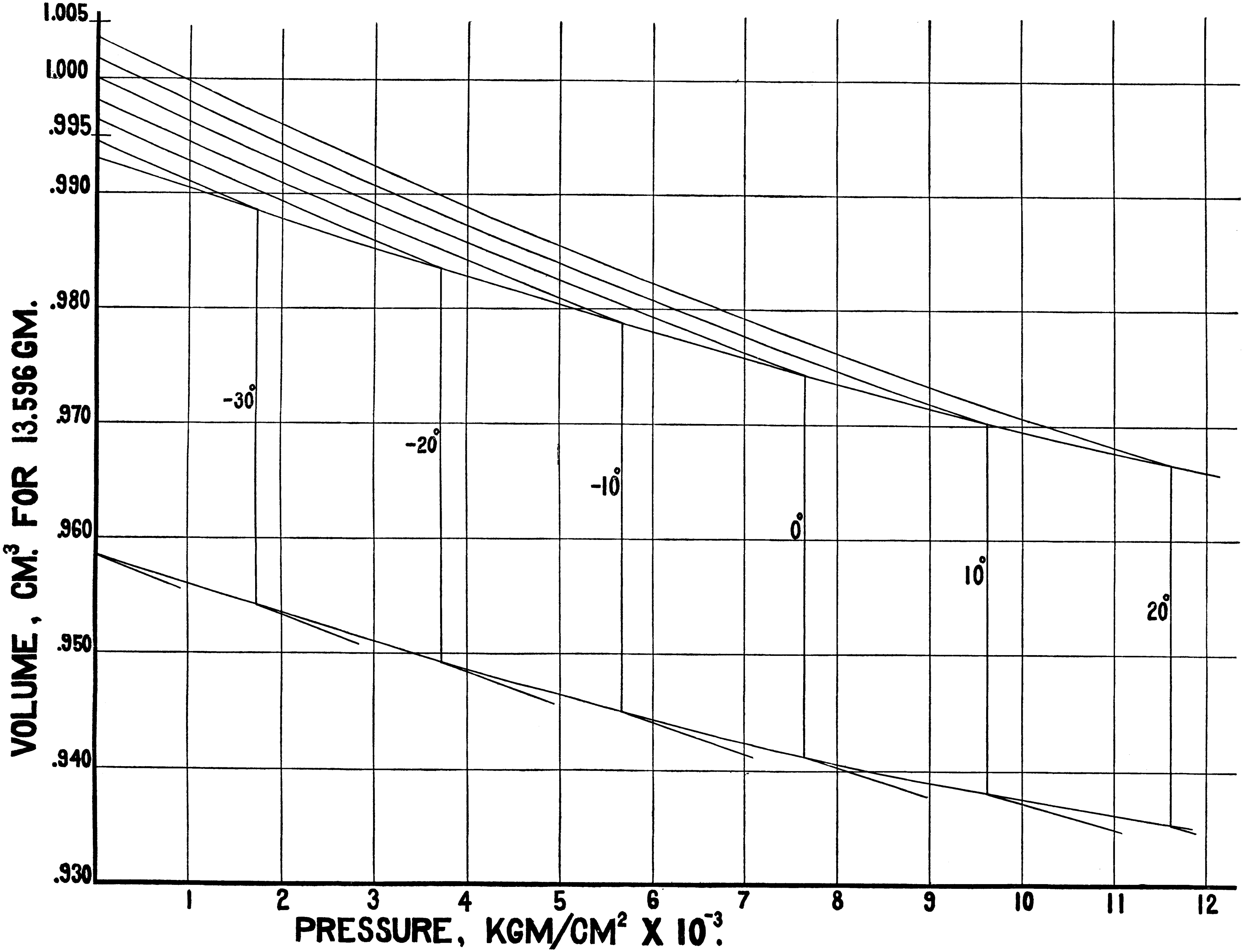

PLATE. Shows the isothermals at 10° intervals of liquid and solid mercury. The upper part of the diagram is for the liquid, the lower for the solid. The initial slope of the isothermals for the solid was not obtained by direct experiment, but was found approximately by a computation.